

# Liquid Air Oxygen Nitrogen

BY

GEORGES CLAUDE

ENGINEER LAUREATE OF THE INSTITUTE OF FRANCE

ENGLISH EDITION CORRECTED AND BROUGHT UP TO  
DATE BY THE AUTHOR

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WITH A PREFACE BY D'ARSONVAL

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## FOREWORD

GR<sup>E</sup>AT as is the present importance of the manufacturing processes connected with the production of liquid air, oxygen and nitrogen, there can be no doubt that it will immeasurably increase in the future, for the known applications of these processes, though already numerous, will not be a tithe of those which cannot fail to be progressively discovered and placed at the disposal of civilisation. This reason, even if no other existed, would have afforded a sufficient inducement for providing a standard work on this subject in the English tongue, an acknowledged want which the present translation, it is hoped, will help to satisfy.

The problem of supplying the ever-increasing demand for nitrogen, in forms suited to agriculture, is a pressing one, to which the relatively excessive cost of nitrogenous manures bears eloquent testimony. Many of the keenest minds of the chemical world have for the last fourteen years been devoting themselves to the solution, which ultimately implies recourse to the practically inexhaustible stores of atmospheric nitrogen in a more or less direct fashion. This in turn implies the solution of the problem of the separation of the air into its constituent elements, and the method of distillation and rectification at very low temperatures, on which both Linde's and Claude's processes are based, has been up till now the most favoured because of the very high degree of purity with which the nitrogen so distilled from the air is produced.

## FOREWORD

The day of nitrogen derived from the air has definitely dawned, and manufactures of its products and derivatives on a grand scale are springing up all over the world, so that within a comparatively short time the old sources of supply of ammonia and nitrates will no longer be the chief and practically only sources on which agriculture can depend for replenishing the ever-depleting stores of nitrogen in the soil. Had the means of producing and distilling liquid air not been developed when they were, as described in the following volume, the day when chemical manufactures shall have rendered the nitrogen famine predicted by Sir William Crookes impossible, would unquestionably have been still in the dim future instead of well in sight and rapidly approaching.

Three reasons added to the above inducement for undertaking the translation of Georges Claude's work on liquid air, oxygen and nitrogen : firstly, because it bears eloquent testimony to the contribution of British scientists both in the discovery and in the practical application of the principles which underlie one of the most difficult problems with which modern science and modern manufactures have had to deal, such testimony being the more important as coming from a foreigner unbiassed by national proclivities ; secondly, because there always has been among Britishers a strong tendency to belittle the work of our own scientific men when compared with that of their Continental competitors, which such testimony must in a measure serve to counteract ; and thirdly, because of the fascinating manner and lucid style in which the subject has been treated by the author, and, it is hoped, successfully preserved in the translation, which, under the circumstances, has been both a privilege and a pleasure to undertake.

THE TRANSLATOR.

# PREFACE

## TO THE FRENCH EDITION

Six years ago Georges Claude asked me for a preface to a work which he was issuing on the subject in question ; while liquid air was still in its infancy. This is how I then expressed myself :

“ What purpose can the liquefaction of the permanent gases serve ? asked the utilitarians in 1877 when they saw us at the Academy of Sciences on December 24th, crowding curiously round Cailletet’s apparatus in our anxiety to catch sight of a trace of liquid air appearing as a cloud for the duration of a lightning flash.

“ Of what use is it ? Why, only to amuse a few scientists, so thought these practical folk.

“ Of what use is it ? Why, to furnish forth a *séance* of legerdemain, to swell up outrageously a guest who should have the pluck to sparkle up his champagne therewith, or even to play a practical joke on a waiter at a restaurant by instantly hardening a tender steak. To a large proportion of the audiences before whom, for the last five years, I have been manipulating liquid air by the quart, it serves for this and nothing more. This is at once too much, yet not enough. It has become necessary to place the matter in its true perspective before the public ; Claude is going to carry out this task in the following pages. He will do so in a style wholly his own, full of imagination though clear and precise. He elects to remain less than academical pro-

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"It is his right—What am I saying? It is, above all, his duty. The public will shrive him—and I also—all the more because of the amount of labour he has bestowed on this very important question; because of the improvements which are due to him in the apparatus for liquefying air, Claude is the best fitted to accomplish successfully the necessary task.

"And now, without wishing to forestall him, I must repeat: Liquefying the air, of what use can this be? Why, firstly to materialise it, to make a liquid of it, which can be seen, touched, and poured from one recipient to another like water. Then by letting it evaporate, this will serve to produce a cold of which no one dreamt, and capable of the strangest applications. Finally it will permit of its being treated as a mixture of two liquids, that is, of its being distilled and separated into its component parts, oxygen and nitrogen, in a similar fashion to that by which distillers separate water from alcohol.

"This is a capital result which must speedily revolutionise lighting, metallurgy, and the chemical industries, sanitation, agriculture, and our notions of matter itself.

"Why? How? Simply by extracting from the atmosphere its oxygen and nitrogen in a state of purity, and its hydrogen from water, or, rather, from water-gas.

"Cheap oxygen is equivalent to obtaining immediately and economically the high temperatures indispensable to lighting with incandescent bodies and to all the metallurgical industries.

"It is equivalent to obtaining carbide of calcium directly—to being able to fuse cheaply the most refractory bodies.

"In sanitation it is equivalent to the purification of the atmosphere, to the purification of water by ozone, to the elimination of smoke, to the disinfection of sewerage, etc.

"In mineral chemistry it is the rejuvenation of the processes for the manufacture of sulphuric acid, of chlorine, of oxygenated water, of ozone, of hydrogen, etc. Cheap nitrogen and hydrogen means the unlimited manufacture of ammonia and the ammonia salts necessary to agriculture.

"Finally, because of the extreme temperatures which these liquefied gases enable us to attain, both above and below zero, we possess an admirable appliance for the purposes of research which will help us to penetrate the mysteries of matter, and, above all, will enable us to become its masters.

"For, as Claude Bernard very justly observed, the object of science is not to explain nature to us, but to make us its masters, which is much more important to the progress and wellbeing of humanity.

"The practical liquefaction of the air is not only a scientific revolution, it is also, and above all, an economic and social revolution."

Through the voluminous sequel which Claude is now adding to his earlier publication on the same subject, we shall see that my forecasts of six years ago have not remained unfulfilled.

The present publication is not only a re-publication, and still less is it a new edition in the strict sense of the term.

It is a new work, possessing entirely original characteristics, and one in which the author is no longer satisfied with being the historian of his subject.

During these five years Georges Claude has never ceased to be a personal contributor to the matter in question. In the following pages will be found an outline of his task and of his personal theories, which have notably advanced our knowledge both from the scientific as well as the

## REFACE

I have closely followed Georges Claude's researches, and I have communicated their important results, as called for, to the Academy of Sciences. The development of these notes will be found in several chapters of this book, and it will be possible once more to judge with what assurance and speed practical applications have sprung up when development is guided and illuminated by scientific theory.

Claude belongs, in point of fact, to that chosen body of experimentalists who unite the positive spirit of the practical man to the spirit of curiosity always wide awake in the man from the laboratory. Theory never seems to him, in point of fact, complete, till the day when it can face victoriously the crucial test of its practical application. Many typical examples of this will be found in the pages of this book. The following are some selected at random :

(1) His machine for producing liquid air by expansion with external work. Theory pointed to the superiority of this method; but in practice it had failed in the hands of clever scientific men and engineers. "*Theory is always right,*" said Claude, and far from allowing himself to be discouraged by the want of success of his illustrious predecessors, he minutely examined in what respect their devices failed to satisfy theory. It was in this way that he discovered lubrication at low temperatures by means of petroleum ethers. The machine thereupon worked, but yielded only one fifth of a litre of liquid air per H.P. hour. "*This is only because theory is not yet satisfied,*" said Claude. He studied the question closer still, and by a very subtle analysis he found that theory was not, in point of fact, complied with. He discovered that at the very low temperature at which his machine was working, the air was not a gas which complied with the requirements of theory. It is not yet a liquid, he said, but it is almost no longer a gas; and thereupon he devised the raising of the temperature of expansion so as to comply with theory. He devised

## PREFACE

liquefaction under pressure, then compound liquefaction, then liquefaction at the critical temperature of oxygen, etc. Theory was satisfied, and the yield of liquid air successively attained 0.66, 0.85, and, finally, 0.95 litres per H.P. hour.

Yes, theory is always right—when in the right hands.

(2) A notable difference exists between the boiling-points of the two constituents of air—oxygen and nitrogen.

Nitrogen evaporates more rapidly than oxygen, on which are founded many processes for the economical separation of the two gases. The minutest details of this evaporation were laboriously studied by Professor Linde, by Baly, etc.—everyone admitted. On the inverse phenomenon, that of the condensation of gaseous air, no one was agreed. Dewar contended that the elements of the air are condensed simultaneously; Linde agreed; Pictet went the length of believing that it was nitrogen, that is, the more volatile, which condensed first. It was, anyhow, most important to be agreed on the question, because if the two gases condensed simultaneously it is evidently necessary to *totally* liquefy the air to separate it into its elements. If, on the contrary, one of the two condensed before the other, partial liquefaction will suffice to effect that separation.

Claude was profoundly surprised at the ante-physical form of Dewar's theory. For, in general terms, the phenomenon of liquefaction is always the inverse of evaporation, and to enable air to behave otherwise it would be necessary that here should indeed exist a very curious anomaly.

Claude made the experiment, with results entirely in agreement with his own forecasts and with the theories of Gibbs, Van der Waals, and Duhem. Consult on this subject Chapter VI on the liquefaction of gaseous mixtures.

Thanks to a most ingenious artifice, Claude took

small proportion of the air to be treated to obtain directly, without antecedent evaporation, a highly oxygenated liquid, holding almost the whole of the oxygen in circulation. This artifice constituted the *backward* return. It admits of the complete separation of all the oxygen in the air under treatment by means of the liquefaction of only one half.

Claude at once went on to the practical application of the improvements he had imagined. The results did not take long to perfect. This liquid air industry and that of separating its elements (realised for the first time in Germany by Professor Linde by means of most ingenious means, which were entirely due to himself) obtained in France a new lease of life through Claude's processes put into practice by "The Liquid Air Company."

These two very different methods have already passed through their practical course, at first as rivals, thereafter, if I am not mistaken, as allies. Personally I shall be very glad of this, for the sake of Cailletet's country, as he was the first to liquefy permanent gases by utilising *expansion*—that remarkable means of producing cold.

I should speak, in closing, of the marvellous results that theory and practice will achieve, and have already achieved, in the industrial production of low temperatures; but the subject is much too extensive, and will be more *à propos* in the new book which Georges Claude is preparing.

I venture to hope that after having read this book every scientific man will understand why we have made it a point of honour, my lamented friend Potier and I, to shield its youthful author from all discouragement.

DR. D'ARSONVAL,

*Member of the Institute of France  
Laborie (Haute Vienne).*



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# PART I

## THE LIQUEFACTION OF GASES

### CHAPTER I

#### FIRST STEPS

It is a very interesting chapter of modern physics which deals with the liquefaction of gases, and before dealing with the problem of the liquefaction of air, which is our real objective, it would be a pity were we to pass over in silence the successive and painstaking efforts which have resulted—but yesterday—in the complete mastery of the liquid and gaseous conditions.

Here, as in the case of so many other questions, theoretical conception has long outstripped its practical realisation.

Physicists, observing that common liquids, under the action of heat alone, resolved themselves into vapours, as fluid and as elusive as gases, and seeing these vapours, by cooling, reproduce with equal facility the liquids from which they came, were thereupon led to ask themselves questions on the subject of gases which nature or chemistry placed in their hands; they have been led to ask if these gases were not also vapours of liquids, of peculiar liquids which were immeasurably more volatile than common liquids, and were subject at far lower temperatures to the tumultuous agitation of boiling.

This conception, however, is not very ancient, for to see its first beginnings it is but necessary to go back as far as Lavoisier; but this illustrious chemist, as a set-off, formulates the statement in words whose audacity and exactitude call for unstinted admiration. At a time when the gases which are most susceptible to condensation had as yet never been seen in liquid form, when the first steps towards liquefaction had not yet been taken, these are the almost prophetic terms in which he did not hesitate to express himself.

“If the earth should find itself all of a sudden placed in very cold regions, such as exist between Jupiter and Saturn, the water which now forms our rivers and seas, and probably the greater number of the liquids which we know, would be transformed into solid mountains and into very hard rocks. The air under this hypothesis, or at least a portion of the aëriform substances which compose it, would doubtless cease to exist in the condition of invisible fluids through the absence of a sufficient degree of heat; it would revert to the liquid state, and this change would produce new liquids of which we have no idea.”

It is thus that ever since Lavoisier's time this belief has taken its place among the fundamental dogmas of physics—the three conditions of bodies, solid, liquid and gaseous—a sequence resulting from the successively more violent action of heat—are susceptible of being inverted when heat is removed.

Modern research has confirmed—in the case of at least all bodies which are not decomposable by heat—that this conception is perfectly legitimate and perfectly general. It is therefore permissible to commence without further preamble by the liquefaction of gases, simply recalling the laws which rule the evaporation of liquids and the condensation of their vapours.



# THE VAPOUR TENSION OF LIQUIDS—SATURATED AND NON-SATURATED VAPOURS.

Here (Fig. 1) is a barometric tube which is filled with mercury and has been turned upside down on its holder so

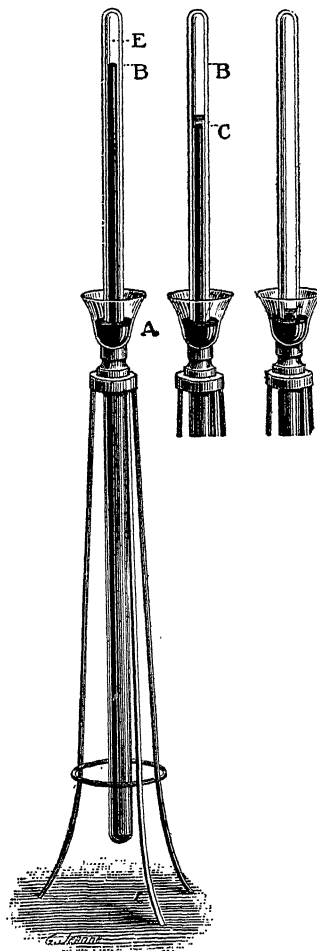


FIG. 1.—Barometric column. FIG. 2.—The mercury is pushed back thus a distance B, C by the vapour tension of the liquid introduced. FIG. 3.—The level of the interior mercury has been lowered down to the level of the exterior through the increasing tension of the heated liquid.

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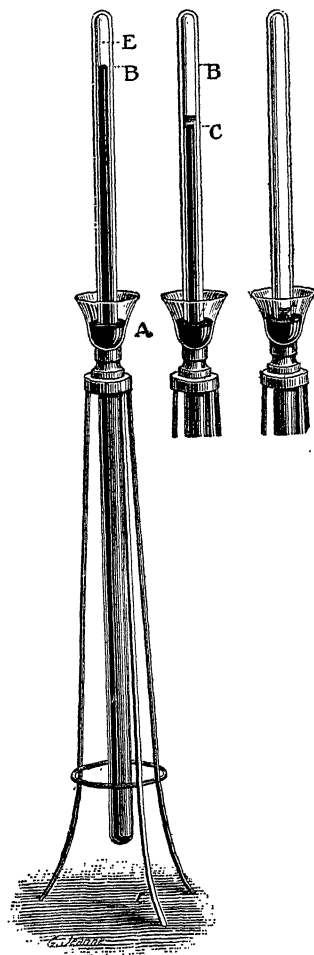


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that there is a vacuum in the space E; we know that the mercurial column A-B measures by its height (160 mm. about) the amount of the atmospheric pressure.

Let us introduce into this tube, by means of a bent pipe, some drops of any given liquid, water, alcohol, etc.

Having reached the free surface of the mercury (Fig. 2) the liquid is evaporated in the vacuum, and the level of the mercury is through the effect of the vapour produced lowered suddenly by a certain quantity B-C, which is evidently a measure of the elastic force or the tension of this vapour under the conditions in question.

Two cases should be considered :

(a) If the liquid which is introduced is in excess it is only partially evaporated. The barometric space E therefore contains all the vapour which it can hold, and is therefore said to be saturated, and the lowering of the level of the mercury is then also as great as possible, and it is interesting to note that this lowering at the temperature in question is then perfectly *determined* and *fixed*, whatever may be the quantity of liquid in excess ; the tension of the saturated vapour at the temperature selected appears, therefore, to be a true physical constant characteristic of the liquid on the same footing as its density and its boiling-point.

(b) If the liquid introduced is completely evaporated, then it is in insufficient amount to furnish all the required vapour. In this case the lowering of the mercurial level, instead of giving the well-defined value which characterised it previously, depends upon the quantity of liquid employed, for it is perfectly clear that if very little liquid is introduced the lowering of the mercurial level can only be slight. The tension of a *non-saturated* vapour does not, therefore, present any defined value, and may attain, in proportion to the quantity of liquid introduced, all possible values from zero to a maximum, which will evidently correspond to the tension of the saturated vapour ; this is also called for this reason the maximum tension, and is the real elastic force of the vapour at the temperature in question. It is this tension

which is meant when vapour tension is spoken of without any qualification.

The notion of non-saturated vapour which has been just indicated should not, however, be forgotten, as it corresponds to a practical case of extreme interest, as we shall have to acquaint ourselves with the fact that gases are nothing else but non-saturated vapours.

#### VARIATIONS IN THE VAPOUR TENSION OF LIQUIDS IN ACCORDANCE WITH THEIR CHARACTER AND WITH TEMPERATURE.

For the same temperature the vapour tension of a liquid is naturally higher the more volatile the liquid.

It is, for example, at  $20^{\circ}$  about 17.4 mm. for water—that is, at  $20^{\circ}$  the mercurial column is lowered by water to the extent of 17.4 mm.; at this temperature it is 44 mm. for ordinary alcohol, 95 mm. for methylic alcohol and 442 mm. for ether, and these figures indicate by their amount itself the order of volatility for these various liquids. On the other hand, for the same liquid, this vapour tension increases rapidly with the temperature. If the barometric tube is progressively heated,\* the level of the mercury is lowered more and more rapidly under the influence of the increasing evaporation of the liquid above the mercury, giving a tension for water of 31.5 mm. at  $30^{\circ}$ , of 92.0 mm. at  $50^{\circ}$ , and 288.5 mm. at  $75^{\circ}$ .

If we continue to increase the temperature, the lowering of the mercury still increases in rate; at a given instant (Fig. 3) the liquid under examination being still supposed to be in excess, the barometric column is depressed by the saturated vapour down to the level of the external mercury of the mercury in the cup. At this instant, evidently the

\* It may be for this purpose enclosed in a glass jacket outlined beneath the figure by a light outline in which can be circulated water or any other liquid which is brought up to the required temperature.

elastic force of the vapour exactly balances the atmospheric pressure; it equals 760 mm.

Now, if we measure the temperature at that exact instant we find it exactly equal to  $100^{\circ}$ , the temperature of boiling water under atmospheric pressure. The coincidence is interesting, and immediately we put our hand on this physical law:

The temperature of ebullition of a liquid under atmospheric pressure is that where the tension of its vapour is just equal to the pressure of one atmosphere.

The laws of Nature have evidently all of them very good reasons for being, but it is so seldom that we are able to discern them that it is worth while to underline the fact when the occasion offers. This is a case in point, for it can be easily understood that it is only when the vapour possesses an elastic force capable of balancing the atmospheric pressure which rests on the liquid that it is possible for it to be given off in big bubbles in accordance with the usual process of ebullition.

So long as the tension of the vapour does not attain this limit the bubbles necessarily cannot be produced, and we have nothing more than superficial and slow evaporation, and not ebullition.

#### THE HEAT OF EVAPORATION.

Let us now consider a liquid heated in the free air. We know that its temperature, which increases without hindrance up to the point of ebullition, suddenly stops when that point is reached, however intense the source of heat may be—and why?

The reason is that the change of physical state on the one hand, and on the other the enormous increase of volume achieved in spite of the atmospheric pressure when gassification takes place, call for a considerable amount of work which entails a great absorption of heat. We can

tion of intense cold which the simple and slow evaporation of water occasions when getting out of a bath.

Nevertheless, so long as the liquid in question which is being heated has not reached the stage of ebullition, the slight superficial evaporation calls for a relatively slight absorption of heat; almost all that is communicated from the source of heat is employed, therefore, in progressively heating the liquid. On the contrary, as soon as ebullition is attained, the absorption of heat demanded for the production of the bubbles becomes enormous; it is only limited by the intensity of the source of heat, and however great this may be, all its energy is thereafter expended in this phenomenon.

The quantity of heat thus called for per unit of weight of the boiling liquid is called its *heat of evaporation*. According to Regnault, this is in the case of water at 100° C. equal to 537 calories per kilogramme.

This is a stupendous quantity.

In fact, these figures mean that to evaporate only, that is to pass from the liquid state at 100° to the gaseous state at 100°, water absorbs, *without being heated*, a quantity of heat five and a half times greater than when passing from the temperature of melting ice to that of boiling! From this point of view, be it noted, as well as from many others, this very remarkable liquid which is water holds by a long way the record, as will be seen from the following table, which gives the boiling-points and the heats of evaporation for a few well-known liquids.

Name of liquid.	Boiling-point.	Heat of evaporation in calories per kg.
Ether . . . . .	35°	90
Acetic acid . . . . .	120°	102
Alcohol . . . . .	78·5°	208
Methylic alcohol . . . . .	66·5°	264
Water . . . . .	100°	537

**Indispensability of cold to the existence of liquefied gases in free air.**—To anticipate somewhat our objective, we can, legitimately, deduce an interesting and obvious consequence from the above.

Let us first remark that it is impossible to heat a liquid *in free air* beyond its point of ebullition, since if we increase the source of heat we can only produce more violent ebullition without raising the boiling-point.

In other words, a pure liquid could not exist under normal conditions in free air at a higher temperature than that of its boiling point.\*

If, therefore, the idea of physicists is correct, which considers gases as the vapours of liquids which are extraordinarily volatile—that is, implicitly possessing at *very low* temperatures the vapour tension of one atmosphere required for ebullition—these liquids could not persist normally, could not *exist* in free air except at very low temperatures.

We conceive in this way the character of the part, foreseen by Lavoisier, which cold is capable of playing in the liquefaction of gases. An essential part, indeed, because, as we shall see later, this effect of cold furnishes the *only* method which is sufficient in itself in all cases to bring about this liquefaction. At a sufficient degree of cold no gas, even helium, could hold out; also, without doubt, physicists dealing with this interesting problem would have got considerably closer to their goal if they had held fast to this idea. No doubt the production of very low temperatures must have appeared to them for very long as one of the supreme difficulties of physics, but had they been more obstinate—and the rewards of the problem were well worth it—without any doubt they would have discovered, to the great advancement of physical

\* Impurities, and especially saline matter in solution, may notably raise the boiling-point, and also incidentally produce the phenomena of unstable equilibrium known under the name of "superbullition."



science, the marvellously simple means which we dispose of now for the production of great cold.

But we shall see shortly what circumstances, very favourable in appearance, occurred to put them off the scent, and direct their efforts in another direction.

### THE INFLUENCE OF PRESSURE ON EBULLITION.

(a) **Effect of diminution of pressure.**—We have seen above that when a liquid is heated in free air ebullition occurs when the vapour tension, progressively increasing, attains a value capable of counter-balancing the pressure of the atmosphere. Now, if we diminish the pressure acting on the liquid by producing in the container which holds it a *partial vacuum*, it is evident that a lesser vapour tension obtained at a lower temperature will suffice to overcome the reduced pressure, and bring about ebullition; the boiling-point will be thus lowered, and will be the lower the more perfect is the vacuum produced.

These circumstances are in certain cases brought about by Nature itself.

At the tops of mountains, for example, the atmospheric pressure is diminished by the height of the column of air left below them by the climbers. One of the facts which impressed itself most on de Saussure during his famous ascent of Mont Blanc, was that on the top of the frozen peak of the giant of the Alps it is barely possible to produce hard-boiled eggs in boiling water, so greatly is its boiling-point lowered.

Better still:

In the high vacua of air pumps the temperature of ebullition of water can be lowered below that of freezing; under these circumstances light boiled eggs would themselves become a myth! And in point of fact it is by no means impossible with a good air pump to maintain on the liquid a pressure of only one or two millimetres; and as at  $0^{\circ}\text{C}$ . the

vapour tension of water is still 4.6 mm., it will be seen that water is still at that temperature to a great extent under the conditions required for ebullition; since its vapour tension is higher than the pressure.

**Refrigerating machines based on evaporation.**—It is evident, therefore, that evaporation realised under such conditions may afford a powerful source of *cold*. If, for example, a bottleful of water is connected with an air pump of sufficient capacity, it begins to boil violently, because with its initial temperature, its vapour tension is considerably higher than the reduced pressure kept up by the pump. Now in this case the heat absorbed by evaporation (p. 7) and carried off by the vapour, not being furnished by a source of heat, can only be furnished by the liquid, which is rapidly cooled, but the pressure being always maintained *below* the vapour tension, notwithstanding its being lowered through cooling, boiling continues, the cooling increases, and at a given moment the liquid is entirely congealed. This very neat physical experiment has served as the basis of very interesting ice-making machines, such as the Carré machine, in which the absorption of the vapour is produced by the well-known affinity of sulphuric acid for water. Such also is the extraordinary machine, a veritable shocker for common-sense, of the appreciated and well-known engineer, Maurice Leblanc, where the function of freezing the water is allotted to a jet of steam. To this jet, acting as a Giffard injector, is entrusted the work of maintaining a vacuum, and it does this in such a conscientious way that it freezes water by tens of quintals an hour, and very economically, too, in the machines made by the Westinghouse Company!

Physics are very partial, as everyone knows, to such paradoxes, and this is not one of the least of their charms.

We have just seen that, when with the aid of an air pump a certain degree of vacuum is maintained over a

liquid, this is compelled to descend to the temperature at which the vapour tension closely equals the reduced pressure kept up by the pump, because so long as this tension is higher ebullition continues, and cooling increases. If, therefore, the liquid is very volatile, that is, preserves down to very low temperatures an appreciable tension, these very low temperatures can be obtained through its simple evaporation *in vacuo*.

For example, sulphuric ether, whose tension at  $-40^{\circ}$  is still higher than 5 mm., can be cooled below this temperature\* by simple evaporation below this pressure of 5 mm.

But, instead of descending very low in temperature through the evaporation of a very volatile liquid under a good vacuum, it is often advisable to attain a more modest temperature with a lesser vacuum. For example, the tension of sulphuric ether at  $-10^{\circ}$  C. being 111 mm., it can furnish this quite respectable temperature through its ebullition in a very poor vacuum, which far less perfect and elaborate air pumps than are necessary in the case of water are quite sufficient to produce. It will be seen, therefore, that to exhaust a rarefied gas down to 2 mm. of mercury the work of the apparatus is not very difficult, and that pumps of very great efficiency are not necessary to effect this, and none are provided in our new proposals.

Looked at in this way, on the contrary, the evaporation of liquids has become one of the most convenient methods known for producing cold; it is employed on a very large scale in the refrigerating industries, where the machines based on this principle are legion, machines using methyl chloride, sulphurous acid, ammonia, carbonic acid, etc.

(b) **Effect of increasing pressure.**—We have pointed out the lowering of the boiling-point of liquid through the diminution of the pressure to which it is subjected. Let

\* Conditionally on the recipient being protected by a suitable insulating covering to prevent the penetration of external heat. (See "Preservation of liquid air," p. 202.)

us; on the contrary, increase the pressure. We shall have to heat it more to impart the higher vapour tension capable of overcoming this pressure, and the temperature of ebullition will rise, and rise all the more the higher the pressure becomes.

Thus water-boils at 199° under the fifteen atmospheres' pressure of steam boilers, and thus in the boilers of the Serpillet cars, where the pressure often rises to fifty atmospheres, the boiling temperature attains 265°. We see that it is easy by adopting suitable means to melt tin in water, and that it is not impossible to even melt lead.

We should remark that this pressure which has to be applied to the heated liquid to cause its temperature to rise is applied without any complication from the liquid itself, because it is established automatically under its influence in the closed recipient, where a pressure is established evidently equal at each instant to the elastic force of the vapour itself.

It should be observed that under these conditions which are those of the production of pressure in a boiler, ebullition cannot be produced so long as the steam is not drawn off, because the vapour tension which is blended in this case with the effective pressure cannot be exceeded. The heat furnished by the furnace, not being subtracted from time to time by the removal of the steam, remains almost completely available for the liquid, whose temperature rapidly rises *pari passu* with the vapour tension and therefore with the pressure, and it is only when, the pressure being sufficiently raised and the steam is withdrawn, that ebullition can occur, because the pressure being reduced slightly through this withdrawal, the vapour tension takes the upper hand. Thereupon the pressure ceases to increase, because the heat furnished by the furnace is drawn off with the steam, and, if the production of steam corresponds closely with the heat imparted, the pressure adjusts itself to the selected amount.

The table given below summarises for water, according to Regnault, the enormous variations in boiling temperature in terms of the pressure itself, this being expressed in atmospheres. As a matter of fact this table was drawn up for quite another object, which was to indicate for each temperature the corresponding vapour tension; but we know that these two tables should only form one, since when the effective pressure is reduced ever so little below the vapour tension, ebullition is at once produced :

Temperature.	Vapour tension in atmospheres.	Temperature.	Vapour tension in atmospheres.	Temperature.	Vapour tension in atmospheres.
80°	0.47	130°	2.67	180°	9.93
90°	0.69	140°	3.58	190°	12.42
100°	1.00	150°	4.71	200°	15.38
110°	1.41	160°	6.12	365°	200.30
120°	1.96	170°	7.84		Caillaud and Colardeau

These results can be represented by curves which are shown in Fig. 4. The respective curves for different liquids which are represented on the same figure though separated one from the other in respect of temperature when considered generally present characteristics which are practically identical. We shall have occasion to return to this when we shall speak of the work of Van der Waals (Chapter V).

**Pressure may be substituted for cold to obtain certain gases in the liquid state.**—We have just seen (p. 8) the impossibility of a liquid existing in free air at a temperature above its boiling-point, from which we inferred that the hypothetical liquids whose vapours are gases could not exist in free air save with very great cold, and the production of very low temperatures may have seemed at that moment an unavoidable necessity of liquefaction.

Now we have just found that pressure is a means of raising the temperature of a liquid beyond, and far beyond, that of its normal ebullition, and a train of reasoning which

has led scientific men of the last century both to many a success as well as to many an unfruitful effort occurs to us in all its attractive simplicity. Suppose the hypothetical liquid corresponding to a given gas is produced, this liquid,

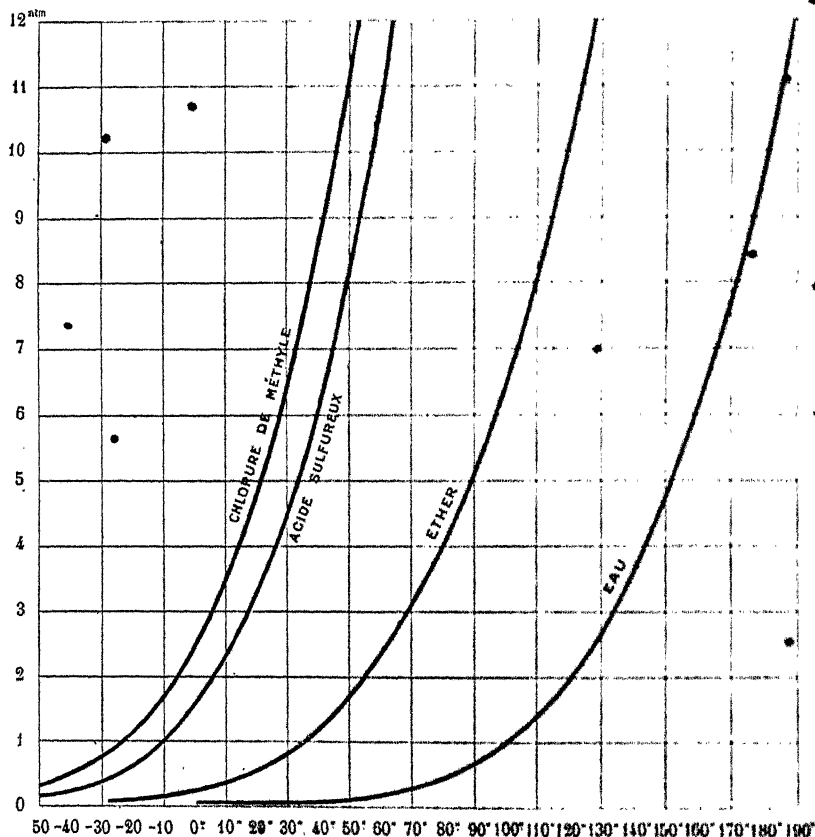


FIG. 4.—Curves showing variations in the temperature of ebullition for various liquids in terms of the pressure.

be it remembered, can only exist in free air at a very low temperature; but if we place it in a closed vessel we can heat it, thanks to the pressure that will be developed. If we proceed in this way up to considerable pressures, enormous if need be, there is no apparent reason why we should not in this way raise the temperature of the liquid in question to the temperature of the room. The existence

of the liquid in question at the temperature of the room should therefore be possible provided it is kept under sufficient pressure, and we can now conceive that, independent of all question of cooling, it will be sufficient to treat the original gas in such a way, under this high pressure, as to bring about its liquefaction.

• We shall see presently what this reasoning is worth; we shall see doubtless all the successes as well as all the disillusion which it has caused for scientific men, but before proceeding further it will be necessary to exactly ascertain what are these conditions "suitable" to liquefaction.

• And in this way we shall arrive at the laws of the condensation of vapours.

#### • A SATURATED VAPOUR SUBJECTED TO A PRESSURE GREATER THAN ITS TENSION IS LIQUEFIED.

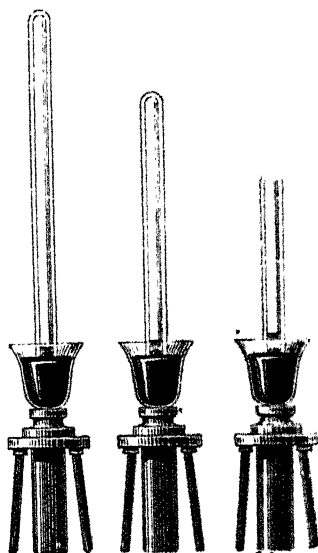
Let us take up our barometric tube again (Fig. 5) at the stage where we last left it (p. 6), that is, at the moment when under the influence of the heat imparted from the external muffle, the mercurial column is depressed by the vapour down to the level of the mercury in the holder, that is, is in equilibrium through the effect of two equal and opposite forces, the atmospheric pressure on one side, which tends to cause the mercury to rise to 76 cm. in the tube, and the vapour tension of the liquid at its normal temperature of ebullition on the other, which prevents it from rising.

It is assumed that the liquid under examination is in excess, that is, that we are dealing with a *saturated* vapour (p. 4). Now, without altering the temperature, let us force the tube down into the cup for, say, 10 cm. (Fig. 6). We provoke by this simple action an exceedingly interesting phenomenon. You may think, and might assuredly think, that the internal mercury would follow the movement, and that its level would be depressed by some centimetres below the external level, and this is what in point

of fact would take place had we to do with an ordinary gas.

Well, nothing of the kind occurs in this case, and the matter is explained as follows:

For were it as you think, the vapour in our tube which up to this point received from the mercury a pressure only equal to the atmospheric pressure, since without its presence the mercury would rise to 76 cm. in the tube, this



Figs. 5, 6, 7.—The progressive depression of the tube does not alter the level of the mercury, but brings about the progressive liquefaction of the vapour.

vapour would be subjected by the disturbance in the level of the mercury to an increased pressure equal to the difference in level. And this is exactly what is impossible, since at the normal temperature of ebullition, which is maintained by the muffle, the vapour only possesses and can therefore only exert an elastic force equal to one atmosphere.

Thus, contrary to what we expected, the mercurial column does not follow the movement; it is in vain for us to depress the tube further and further. The internal



level of the mercury is maintained at the level of the external mercury and the volume of the gaseous chamber is *reduced more and more*, since there can be no question of *compression*, for the interior pressure remains always equal to the atmospheric pressure.

What does this mean?

It clearly can only mean one thing: that is, that as we progressively depress the tube in its sheath the vapour condenses, that is, progressively liquefies.

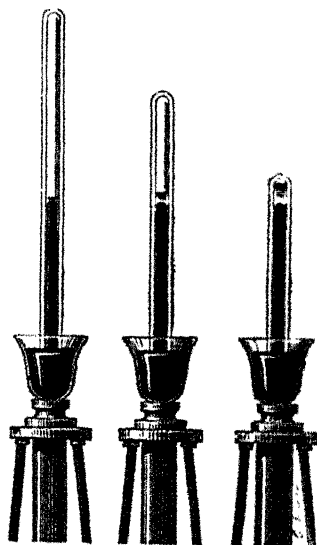
In fact, that is exactly what occurs, and during the depression of the tube we can see a liquid pouring over the walls.

The more we depress the tube, the more the amount of liquid formed increases (Fig. 7).

If the sheath is sufficiently deep, as is shown in Fig. 1, to allow the tube to be entirely plunged into the same, as soon as its top reaches the level of the external mercury the vapour chamber completely disappears and the whole of the initial liquid is reconstituted.

The preceding experiment has been carried out to clear our ideas at the temperature of normal ebullition. We are going to repeat it just as successfully at any selected temperature, and the excuse for its repetition is that we shall thereby obtain an instructive lesson. Let us work, say, at  $60^{\circ}$ , the liquid under examination being still water. At this temperature the mercury rises very high in the tube (Fig. 8). The height of the column of mercury is 611 mm., which corresponds in accordance with Regnault's table to  $760 - 611 = 149$  mm., about the tension of water vapour at this temperature. Let us depress the tube into its sheath: for the same reasons as above, the mercurial column remains unmoved at 611 mm., however great the depression (Figs. 8, 9, and 10), and the walls of the tube are covered with water as before. The interesting fact is the following: Just now, at  $100^{\circ}$ , the liquefaction of the saturated water

vapour was accomplished under a pressure equal to the height of the wholly depressed barometric column, viz. in this case 760 mm.; at 60° the mercury only exercises on the vapour a pressure of  $760 - 611, = 149$  mm., equal to the vapour tension. Therefore liquefaction takes place under a much lower pressure than before. It would be still lower, that is, 17.4 mm., if we worked at 20°, and on the contrary much higher, or 2718 mm., = 3.57 atmospheres, if we worked at 140°.



Figs. 8, 9, 16.—Liquefaction at a lower temperature is effected under a lower pressure.

**Conclusion.**—The liquefying of a vapour is effected all the more easily, under a pressure all the lower the lower is the temperature. This is the general law, and we can select for liquefying not only vapours but gases themselves, with a combination of cold and pressure which will render signal service in a practical fashion.

To resume, if we endeavour to increase beyond its proper tension the pressure exerted on a saturated vapour, this vapour is liquefied and the phenomenon proceeds under *the same pressure* (let us make a note of this) till complete liquefaction.

**Reversability of Ebullition and Liquefaction.**—We have still much to learn from the very simple experiment which has contributed the whole of our present knowledge.

The tube being depressed down to the point where the gaseous chamber disappears through complete liquefaction, let us lift it up progressively (Figs. 8, 9, and 10). The phenomenon is inverted.

The liquid commences to *boil* and the vapour is reconstituted as soon as we lift up the tube, but the mercurial level in this case also remains always invariable so long as an excess of liquid is present. The interchangeability of the phenomena shows us clearly that ebullition and liquefaction are in fact the exact inverse of each other, that they occur at the same temperature under the same pressure, with only a slight excess in the vapour tension over the pressure in the case of ebullition, and of the pressure over the tension of the saturated vapour in the contrary case.

In other words, a liquid maintained at a certain temperature possesses a well-defined vapour tension; if the pressure in the enclosure by which it is contained be maintained slightly below this tension (as in the case of the progressive lifting up of the tube) ebullition takes place; all the liquid is vaporised progressively at a constant temperature.

If, on the contrary, the pressure is superior to the vapour tension (when the barometric tube is depressed, or compression of saturated vapour in a closed vessel of the same temperature occurs), the vapour is condensed and liquefaction takes place. Thus the temperature of ebullition of a liquid under specified pressure is also the temperature of liquefaction of its saturated vapour under the same pressure.

#### THE HEAT OF LIQUEFACTION.

On the other hand, it is not only in certain of its manifestations that the phenomena of liquefaction is the inverse of that of ebullition. We have seen (p. 17) that one of the

essential facts that characterise the latter is the absorption of an enormous quantity of heat called *heat of evaporation*. Now, at the moment when vapour reverts to the liquid state all this heat is naturally placed at liberty; this is the heat of liquefaction; it is evident because of its very origin that this heat of liquefaction is exactly equal to the heat of evaporation, conditionally, however, that the liquefaction takes place under the same pressure, and, therefore, at the same temperature of ebullition.

Thus a vapour, when being liquefied, gives up a great quantity of heat; it is evidently necessary to withdraw this heat progressively as it is given up otherwise liquefaction will be arrested. This was in the preceding experiment (p. 5) the part played by the auxiliary liquid which circulated in the muffle attached to the apparatus, which maintained the temperature constant at the selected degree. Otherwise, at the moment that the tube was depressed, the heat liberated by the commencement of liquefaction would tend to raise the tension of the liquid, would stop liquefaction, and nullify all our conclusions. All these experiments, as well as those following, must be made at a *constant temperature*.

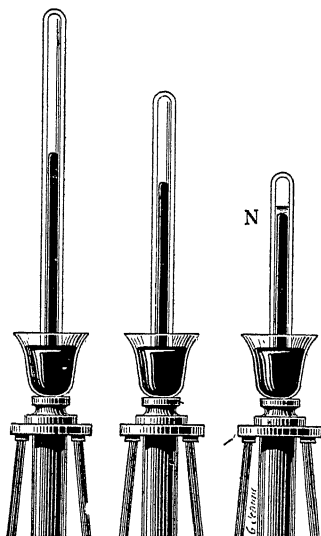
The enormous setting free of heat by a vapour which is being condensed is the basis of heating by steam. We shall also see (Chap. XIII) for what services we are indebted to it, when we shall deal with the extraction of oxygen from the air by means of liquefaction.

#### **A NON-SATURATED VAPOUR SUBMITTED TO PRESSURE IS COMPRESSED LIKE A GAS TILL IT BECOMES A SATURATED VAPOUR.**

The experiments we have been making teach us that, quite contrary to a gas, a saturated vapour is incompressible in the correct signification of the term. When we try to diminish its volume at a constant temperature, no contrac-

tion occurs in the case of gases but liquefaction takes place, while the pressure does not increase. A saturated vapour is, however, an elastic fluid in this sense, for if it is not compressible, it is at least—happily for the steam engines—expandable on account of its elastic force. A non-saturated vapour behaves quite differently.

• We know (p. 4) that a non-saturated vapour can be obtained by passing into the barometric vacuum of our



FIGS. 11, 12, 13.—The barometric tube holding in this case a non-saturated vapour the mercury is depressed, when the tube is depressed up to the moment when liquefaction occurs.

experimental tube an insufficient quantity of liquid which is entirely evaporated and depresses the mercurial column, no longer by a fixed and determined quantity corresponding with the tension of saturation for this temperature, but always some lesser quantity all the smaller, the less the quantity of liquid introduced.

The elastic force of a non-saturated vapour is therefore always less than that of a saturated vapour at the same temperature. Now let us depress our barometric tube

find on this occasion (Fig. 12, 13) that instead of being maintained at the same level the mercury here is *progressively depressed*—is lowered progressively—submitting, therefore, the internal vapour to a pressure *more and more intense*. Under the increasing pressure which is exercised on it the vapour is unavoidably *compressed*, and we observe in fact that if the internal mercury is much depressed, it is depressed less than the tube; consequently, its vapour chamber diminishes, but in this case without liquefaction.\*

Thus, quite contrary to a saturated vapour, a non-saturated vapour is a compressible fluid.

On the other hand, the elastic force of a vapour, instead of being invariable, *progressively increases*, since it depresses the mercury less by an increasing quantity.

At a given moment at N (Fig. 13), the mercury, by descending, reaches the level which it would have reached immediately if sufficient liquid had been introduced—that is, if the vapour had been saturated.

At this moment the vapour has, therefore, acquired an elastic force equal to that of a saturated vapour, that is, it has become itself a saturated vapour; and this was to be foreseen, because, if the quantity of liquid was insufficient at first starting to saturate all the space corresponding with the barometric chamber, it can well saturate the space, which has become smaller through compression. Starting from this moment we return evidently to the limits of the previous case; if we continue to depress the tube, the mercury ceases to descend and liquefaction occurs.

#### **NON-SATURATED VAPOURS DEPART FROM MARIOTTE'S LAW THE CLOSER THEY APPROACH SATURATION.**

In this way, therefore, a non-saturated vapour differs from a saturated vapour and approximates to a gas in that

\* We shall see (Chap. XVI) that gaseous mixtures in this respect.

it is compressible, and that when its volume diminishes its elastic force increases.

This analogy with gases nevertheless does not exclude small differences. In gases such as air, hydrogen, carbonic oxide and even carbonic acid, the Abbé Mariotte has laid down the condition by which their compression is governed in the famous law which bears his name: At a given temperature the volume of a gas is in inverse ratio to the pressure to which it is subjected—in other words, the volume of a gas is reduced to a half if the pressure is doubled, to a third if it is trebled, etc.

Now, with a non-saturated vapour, the reduction in volume is effected quicker than the increase in pressure, and all the more rapidly as the vapour approaches saturation. This is a gradation which is dear to nature, and for which we should have been prepared, since at saturation Mariotte's law no longer applies at all, as the volume diminishes without limit *without increase of pressure* down to total liquefaction.

The further, on the contrary, a vapour is from saturation, whether this occurs by the introduction of less liquid in the barometric vacuum, or that with an equal or insufficient quantity of liquid the vapour is increasingly heated, the more exactly we find the law applies. This appears to point out to us that a vapour puts on a *gaseous state progressively more perfect* the further it is removed from saturation.

Let us compare this fact to a very interesting circumstance revealed by the exhaustive study of compressibility in gases, and we shall see in outline some of the doubts expressed with respect to their nature, at the commencement of these lines.

For gases, also, in point of fact, Mariotte's law is only approximately true. In their case also, with, however, the exception of hydrogen and helium, the reduction of volume

is *accelerated* as compared with the increase of pressure. For certain gases, no doubt—oxygen, nitrogen, air, carbonic oxide—the discrepancy is very small; it had escaped the analytical genius of Arago, and it required for its determination all the marvellous precision of the master experimenter, Regnault.

In the case of others, on the contrary—carbonic acid, sulphurous acid, acetylene, chlorine—the discrepancy is very great; carbonic acid is reduced at 15 atmospheres' pressure to the volume which corresponds to 16 atmospheres if Mariotte's law were exactly applicable thereto; sulphurous acid at 2 atmospheres already reveals a discrepancy which is more notable still.

Further, the lower the temperature the more the discrepancies are accentuated.

If we compare all these facts, and we note that all ordinary characteristics of gas are met with, likewise in non-saturated vapours and inversely, the *conclusion seems inevitable*: "Gases are nothing but non-saturated vapours which are more or less removed from saturation."\*

And the more or less perfect fashion in which Mariotte's law applies to each gas at a given temperature appears to be a criterion which gives a measure of the distance of a gas from saturation, and informs us, therefore, very exactly, of its greater or less aptitude for liquefaction. As to this, we are at last able, after what has preceded, to imagine two processes for bringing liquefaction about.

### LIQUEFACTION BY SIMPLE REFRIGERATION.

Let us consider a gas submitted to *the atmospheric pressure at the temperature of the environment*.

\* We shall see, however, another definition of the gaseous state proposed by Andrews which is preferable theoretically, and would tend to refuse the character of gas to almost all the gases we know, sulphurous acid, carbonic acid, chlorine, etc.



As it is in communication with the free air, its elastic force is evidently equal to one atmosphere.

As it forms the vapour of an eminently volatile liquid, the tension of saturation corresponding to the temperature of the environment will equal several atmospheres.

Therefore, the gas in question—we are here only repeating ourselves—is a vapour far removed from saturation.

But let us *cool it* progressively.

The tension of the saturated vapour corresponding to these lower and lower temperatures is more and more feeble (p. 6), and as the tension inherent in the gas remains always equal to 1 atmosphere, it follows that, on account of the cooling, the interval between this gas and a saturated vapour is always diminishing; the gas approaches more and more to saturation. It attains it when the temperature reaches the degree where the tension of saturation is also that of 1 atmosphere. Sufficient cooling has therefore transformed the gas into a saturated vapour, and if we endeavour to carry the cooling still further, the atmospheric pressure becomes too much for the vapour tension and *liquefaction is produced*.

If the atmospheric pressure continues to act on the gas, thus maintained at a temperature a little under that which corresponds to the saturation tension of one atmosphere, liquefaction will continue naturally until the whole of the vapour disappears. If this, on the contrary, were contained in *closed* vase and subjected to this temperature, liquefaction, which would then have the effect of reducing the internal pressure, would only continue sufficiently to bring back the vapour to the tension of saturation corresponding with the temperature.

Such is the mechanism of liquefaction by simple cooling, and we have already pointed out (p. 8) that there is no limit to the efficiency of this process, that by its means the

liquefaction of the most refractory gases may be brought about providing the cooling is sufficiently powerful. The regular and rapid lowering of the vapour tension with the temperature is in fact an absolutely general phenomenon, and there always exists in the case of all gases a temperature sufficiently low at which the tension does not exceed that of one atmosphere.

Monge and Clouet appear to have succeeded by means of this process, as far back as the end of the eighteenth century, with one of the first liquefactions mentioned in the history of physics. By causing a stream of sulphurous acid

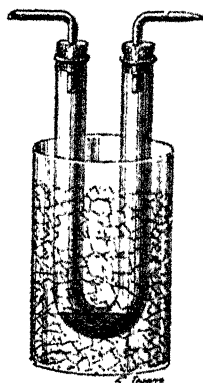


FIG. 14.

to pass through a U-shaped tube (Fig. 14) immersed in a refrigerating mixture of ice and salt, they saw this tube little by little being filled with a colourless very mobile liquid wholly resembling water, viz. liquid sulphurous acid.

In point of fact at  $-10^{\circ}\text{C.}$ , a temperature easily attained with a mixture of ice and salt, the saturation tension of sulphurous acid is only equal to 0.9 of an atmosphere (about). The gaseous sulphurous acid is only able to present to the atmospheric pressure in the U-tube an insufficient elastic force, so it liquefies. The density of liquid sulphurous acid is about one and a half times that of water.

Placed in an open vase in the free air, its temperature

fixes itself, in agreement with theory (p. 7), at  $-8^{\circ}\text{C.}$ , a temperature at which its vapour tension equals 1 atmosphere. It is often the practice in the lecture room by its means to make an experiment which shows in the most striking manner the impossibility for the most powerful sources of heat to change in the slightest the temperature of ebullition of a liquid in the free air. Let us thus place in a heated furnace a capsule full of liquid sulphurous acid. The temperature of this liquid will remain at  $-8^{\circ}\text{C.}$ , being kept there by the rapid evaporation, and the proof, which is visible to the whole audience, and very impressive, is that if we pour water into this liquid it is instantaneously congealed, and that we can take out of this furnace some morsels of ice.

At the temperature of  $20^{\circ}$ , in steel flasks where it is stored for industrial uses, and specially for its employment with refrigerating machines (p. 12), the vapour tension of sulphurous acid is about 3.2 atmospheres.

The same process has been employed by Gayton de Morveau for the liquefaction of ammonia gas but with this gas it is only at  $-38.5^{\circ}\text{C.}$  that the saturation tension is reduced to 1 atmosphere.

The mixture of ice and salt, which can only produce as an extreme minimum  $-21^{\circ}$ , would therefore be in this case quite powerless. Gayton de Morveau owes his success to the use he made of the mixture of ice and chloride of lime, which produces a minimum temperature close to  $-50^{\circ}\text{C.}$

The appearance of liquid ammonia is identical with that of water, the same as sulphurous acid and many other liquefied gases.

Its temperature in the free air is  $-38.5^{\circ}$ , which comes to the same thing as stating that at this temperature its vapour tension equals 1 atmosphere.

At  $20^{\circ}$  the tension equals 8.5 atmospheres, hence it is

pressures of this magnitude that the metallic bottles in which it is stored have to resist.

In a similar fashion cyanogen can be liquefied at  $-20^{\circ}$  C., and chlorine at  $-24^{\circ}$ , a temperature at which it is transformed into a liquid of a magnificent yellow gold colour.

### LIQUEFACTION BY SIMPLE COMPRESSION.

A gas at the atmospheric pressure is a vapour far removed from saturation—let us repeat this for the hundredth time; but if we drive increasing quantities of this gas by

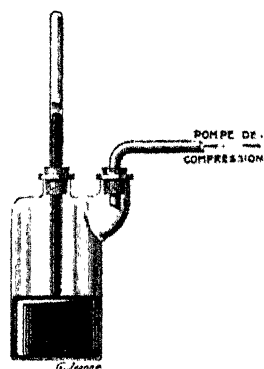


FIG. 15.—The first experiment in the liquefaction of gases (Van Marum, 1792).

means of a pump into a closed vessel whose temperature is maintained constant, the pressure progressively increases in accordance with Mariotte's law.

*There must come an instant* when the elastic force of the gas thus progressively increased becomes equal to the tension which the saturated vapour at this temperature would possess, at which, therefore, the gas itself enclosed in the vessel will be transformed into a saturated vapour. *There must come*, we have stated; but it is not without reason that we have underlined in this way the uncertainty of the result, because the tension of saturation of certain gases at the ordinary temperature is *infinite*.

But if we suppose that with the gas under experiment we shall have the good luck to attain saturation by simple increase of pressure, we know that from this moment all additional increase in the elastic force of the gas is impossible, so that the pressing of an additional quantity of gas into the closed vessel will reduce a precisely equal quantity to the liquid state; from this moment liquefaction will produce itself in a continuous manner, in proportion to the pumping. It is by this method that the first known liquefaction was accomplished, and, like in so many other cases, it was brought about by accident.

The celebrated Van Marum was verifying about 1792, in connection with ammonia gas, the exactitude of Mariotte's law. He had enclosed for the purpose a certain quantity of this gas in a graduated bottle, in connection with which mercury could be pumped, so as to compress the gas (Fig. 15). At first the experiment worked in agreement with the anticipations of the experimenter, when to his great surprise the rise of the mercury was accelerated, and the gas was converted into the unexpected form of a few drops of a limpid liquid. At the ordinary temperature, in point of fact—that is, at  $15^{\circ}$  C.—the tension of saturation of ammonia equals only 7.2 atmospheres, and as the pressure in Van Marum's apparatus could easily have attained this, the result was inevitable.

**Faraday's Experiments.**—It is only the first step that tells, so they say, and this is particularly true nowadays in scientific matters. These lines were written amid the clamours of emotion provoked by the exploit of Orville Wright establishing the record of 1 hour 15 minutes in aviation, which the beginning of the present year has seen lowered to a few minutes; indeed how common will this exploit appear to be before very long.

Nevertheless, nigh upon half a century had elapsed since the genial prophecy of Lavoisier, an almost sterile

half century, marked only by the isolated successes of Monge and of Gayton de Morveau, when in 1832 one of the most eminent physicists that the world has produced attacked the question.

At this period Faraday was still only the modest demonstrator of Humphry Davy. He was experimenting under the directions of his master on the hydrate of chlorine, a crystallised compound which forms chlorine with water when this is passed through it at a low temperature. With the object of studying the action of heat on this compound, a few crystals were introduced in the

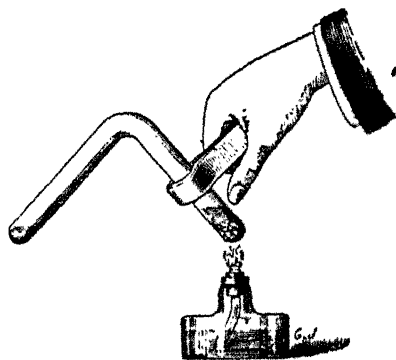


FIG. 16.—Chlorine is liquefied by Faraday.

sealed end of a glass tube of the form of a V, upside down, (Fig. 16), then the other end was in its turn sealed with blow-pipe. Subjected to the action of a gentle heat, the crystals melted, some yellow-green vapours were given off, and a yellow liquid covered the unheated end with its oily drops.

It is stated that in the course of the experiment Dr. Paris, a friend of Davy, coming into the laboratory, scolded the young demonstrator, a little, over the oily drops which were showing in the tube, and which in his estimation evinced a deplorable carelessness. It is added that Faraday, being himself interrogated, made no reply at the time

but the following morning a brief note reached the severe doctor:

“Your oily drops were only liquid chlorine.

“MICHAEL FARADAY.”

The experimenter was worthy of the chance which thus favoured him. Another would have stopped there. Faraday, on the contrary, descried a vëry rich vein which was well worth exploring and followed up to the end. An operating method of remarkable convenience had just been revealed to him; he did not cry halt till he had applied it to all similar cases. Instead of producing the gases to be liquefied in separate apparatus, and then pumping them into the vessel where liquefaction was to take place by means of pressure pumps, both complicated, inconvenient, and changeable, it was sufficient thereafter for him to produce in the vessel itself, by means of an appropriate reaction, increasing quantities of the gas to be studied, which in this way compressed itself to the point of liquefaction in the cool branch, where, because of the lower temperature, the tension of saturation was lowered.

• Let us remark, in passing, that Faraday was realising in this fashion a novel application of the principle of the condenser, to the discovery of which is attached the name of the illustrious engineer, James Watt.

This method, on the other hand, was not without some risks, as on many occasions in the course of his experiments Faraday was injured, even in his eyes, by the bursting of the tubes. But these are minor inconveniences, the current coinage of scientific research, quickly forgotten in the intense satisfaction of a successful experiment; and Faraday could not be the passionate experimenter that we know him to have been, had his ardour been cooled by such rifles.

It is thus that during this memorable year, 1823, hydro-

chloric acid and sulphate of iron furnished sulphurated hydrogen, reduced afterwards to a liquid state by a pressure of 17 atmospheres at the temperature of  $10^{\circ}\text{C}$ ; that mercury and sulphuric acid produced sulphurous acid, liquefied at  $7.5^{\circ}\text{C}$ . under a pressure of 3 atmospheres; that protoxide of nitrogen itself, resulting from the decomposition of nitrate of ammonia by heat, was liquefied under 50 atmospheres; that finally, cyanogen under 37 atmospheres, and carbonic acid under 36 atmospheres completed the list of Faraday's successes in this magnificent excursion. It was enough to whet his appetite, and we shall see presently that he did not stop there.

Many years later this very simple process of Faraday's received an interesting modification, from the point of view of the purity of the gases experimented on, from Melsens. It is well known that wood charcoal possesses the curious property of absorbing readily enormous quantities of different gases, and of allowing them to escape through the lowering of the temperature. This property is subject, even at low temperatures, to considerable augmentation, and we shall have occasion to mention (Chap. X) some extremely interesting applications which are founded on this fact. Now, instead of placing in Faraday's tube the various reagents mentioned above, which could only furnish damp gases, and often mixed with various impurities, Melsens had the idea of placing in the branch to be heated some wood charcoal saturated with the gas to be liquefied, which could in this case have been previously purified with all the care desirable.

**Thilorier's Apparatus.**—In the same way, Faraday's tube could only furnish extremely small quantities of liquefied gas. To be able to comfortably study the properties of these singular bodies it is indispensable to possess them in larger quantities.

To this end Faraday's apparatus received at the hands



of Thilorier an ingenious transformation; it has become possible to bring about the liquefaction of certain gases, and more especially of carbonic acid in considerable masses. Carbonic acid is nowadays a product extensively used. Wine merchants and brewers have taken it under their high protection, which ensures the future of a scientific product effectively in quite another way from all the services it may render in the laboratory. It can, therefore, be

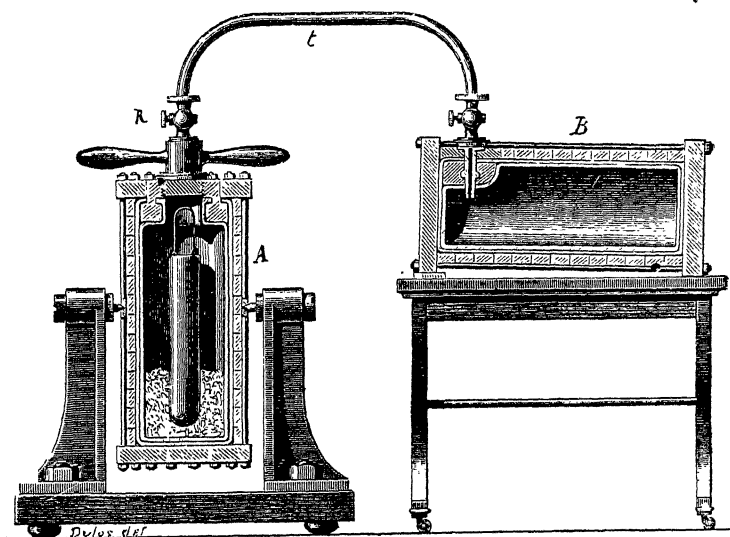


FIG. 17.—Thilorier's apparatus.

procured to-day quite easily in commerce, and Thilorier's apparatus is rather out of fashion.

This apparatus is at bottom only a kind of Faraday tube of large capacity. It was at one time made of cast iron, but in consequence of an accident, which occurred in 1840 at the School of Pharmacy, and which cost his life to the demonstrator Hervy, it has been transformed into the following form by Donny and Mareska.

Two corrugated copper cylinders, lined internally with lead, play the part of the two branches of Faraday's tube.

One, to the left of the figure, is suspended from trunnions and receives the substances, which through their reaction will produce the required gas; such as on the one side a certain quantity of bicarbonate of soda, and on the other side sulphuric acid in a tin capsule.

In the right-hand recipient the gas which is produced will be liquefied.

To put the apparatus in action, the left-hand cylinder A, having received the substances above indicated is closed; then oscillations of increasing amplitude are communicated to it around its trunnions, and ultimately it is completely overturned, so as to send the whole of the sulphuric acid on to the bicarbonate. The reaction takes place, clouds of carbonic acid are given off, and this gas is strongly compressed through the narrow limits of the space at its disposal; nevertheless, it does not liquefy itself at once, because at the temperature at which it is given off its tension of saturation is enormous. But if we then unite the two recipients by the pipe "I," shown at the upper part, and if we open the valve R, the gas passes into the right-hand cylinder and is liquefied under a pressure, which at 15 is still as high as 50 atmospheres. We see that the pressures evolved are quite respectable, and that it is not without reason that the apparatus is strongly constructed.

The operation finished, if we open a valve connected with B, the liquid which has been formed escapes with violence; and an abundant evaporation ensues, the enormous absorption of heat corresponding therewith, immediately effects the cooling of the non-evaporated portion below its congealing point and transforms it into white *snow*, altogether similar to ordinary snow, and which we can collect, to the frequent accompaniment of *electric sparks*, due to intense friction, by directing the jet into a duster rolled into a hollow cone.

This result is not at all surprising.

**Some properties of solid carbonic acid.**—We know, in point of fact (p. 7), that left to itself in free air liquefied carbonic acid must descend to a temperature capable of reducing its tension to 1 atmosphere. Now, this temperature is not less than  $-79^{\circ}\text{C.}$ , and as the point of congelation of carbonic acid is only  $-56^{\circ}\text{C.}$ , it follows that the portion which is not evaporated must become solid. Liquid carbonic acid *does not therefore exist* at atmospheric pressure, and the snow that it forms, different from ordinary snow, evaporates without melting.

If this snow is placed in a closed vessel, such as a sealed glass tube, its spontaneous evaporation, thanks to taking up heat from the environment, raises the pressure progressively. At a given moment the pressure reaches 5 atmospheres, the temperature of fusion of carbonic acid, *i. e.*  $-57^{\circ}\text{C.}$  is reached, the rise in temperature experiences a temporary halt, and the snow is transformed into a liquid which can be again congealed, but this time with the appearance of a transparent block of ice, by plunging the tube for a few instants in carbonic acid snow in the free air.

•These experiments naturally require to be conducted with prudence, on account of the considerable pressure which may be called into play.

Taken between the fingers the carbonic acid snow does not produce the intense sensation of cold which might be expected from its temperature of  $-79^{\circ}\text{C.}$  This circumstance is due to the rather imperfect contact between the snow and the skin, which is proved by the fact that if, as Thilorier did, this snow is mixed with ether, the paste thus obtained at  $-79^{\circ}\text{C.}$  acts on the fingers just like a violent burn if they are plunged in it. Nevertheless, the pain is not always immediate and violent by reason of a species of anæsthesia which is often produced by cold.

The author recollects in this connection that he did not

get out of one of his first skirmishes with low temperatures with the honours of war.

He was occupied in 1897 with researches on the solidification of acetylene, which he was carrying out precisely with the aid of Thilorier's mixture, when at a given moment he had only just time to catch the apparatus with his hands, as its complicated and cranky supports had suddenly given way. Whilst he was reflecting on the unfortunate situation the cold was accomplishing its work surreptitiously, and when they came to his help his two palms were turned into blocks of stone, which were relieved hours after—but in a less painless way—inside two enormous wadded surgical bags.

The mixtures of alcohol and solid carbonic acid are particularly treacherous in this connection. The sensation of cold is not intense when you plunge the finger, or even when you put some in the mouth. D'Arsonval made a curious experiment by immersing in alcohol and cooling gradually with carbonic acid the body of a guinea-pig, who noticed nothing and continued unmoved nibbling his carrot down to the precise instant when he was transformed into a rigid block, and his jaws could move no longer.

By evaporating *in vacuo* this semi-fluid paste we can obtain in conformity with our explanations (p. 11) a very low temperature, reaching down to  $-110^{\circ}\text{C}$ .

This remarkable result, attained with relatively little trouble as far back as 1840 by means of Thilorier's apparatus, enabled Faraday to advance a new and glorious stage further with the problem of liquefying gases.

#### LIQUEFACTION BY SIMULTANEOUS COMPRESSION AND REFRIGERATION.

**Faraday's later experiments**—In his first essays we have seen (p. 30) that Faraday only called upon compression to act upon the gases he wished to liquefy. This fact is

rather singular, because the experiments previously mentioned by Monge, Clouet and Guyton de Morveau, and the almost identical ones of Bussy carried out in 1821, already demonstrated quite clearly that cold is equally a powerful means of coercion when applied to gases.

However this may be, Faraday took up in 1845 the idea, already conceived but insufficiently worked out by Colladon, and afterwards by Natterer, of combining the two means, and of attacking in this fashion the problems which had resisted up to that time the sagacity of experimentalists.

We have explained before in the text (p. 18), the foundation of this method, by pointing out that the lower the temperature at which we work, the less elevated this tension of saturation of a gas, and the less is the pressure required to obtain liquefaction. We have even stated (p. 9) that cold alone will always suffice for the liquefaction of any gas, but you must then descend to a temperature, sometimes excessive, where the pressure of liquefaction of the gas in question is reduced to one atmosphere. If, on the contrary, pressure is called in to help the cold, it will only be necessary to descend to a temperature which will always be much closer, where the tension of saturation is lowered down to the pressure within the capacity of the apparatus which we are using.

In other words, instead of being compelled to wait for an extreme cold or for enormous pressures, it will be generally far more convenient to operate with both a moderate pressure and a less intense cold. And if, on the other hand, we employ high pressures and extreme cold, we dispose of a powerful method, capable of forcing the most rebellious gases to capitulate.

This is precisely the process applied by Faraday with the help of the powerful means of action afforded by the ebullition under reduced pressure of Thilorier's mixture.

And such was his confidence in this device, that he thought neither more nor less of reducing to the liquid form both hydrogen and oxygen, which were notorious at that time for their resistance to the efforts of physicists.

In this new apparatus, Faraday gave up the compression of the gases to be liquefied by auto-accumulation, for the gases on which he proposed to experiment, and specially hydrogen, oxygen and nitrogen, did not always readily lend

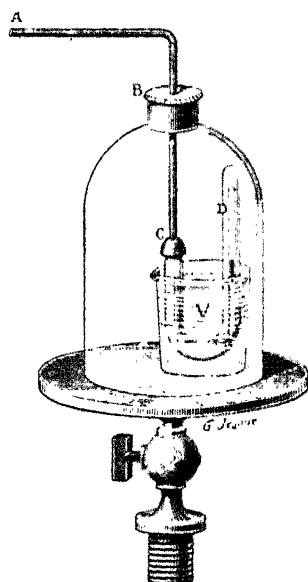


FIG. 18. -- Faraday's second apparatus.

themselves to treatment, in a pure condition in his primitive apparatus.

Here (Fig. 18), the gas under experiment, purified and dried, passes successively into two pumps, which increase the pressure first to 16 to 20 atmospheres, then, if necessary, up to 50; it is then passed (Fig. 18) into a U-tube enclosing a small compressed air pressure-gauge *b*, designed to measure the pressure at each moment by the displacement of a mercurial index in a capillary tube full of air. The U-tube is surrounded with Thilorier's refrigerating mixture,

and if necessary the whole apparatus may, as shown in the figure, be placed under the bell of an air-pump, so as to lower the temperature down towards  $-110^{\circ}\text{C}$ . This is measured by a pure alcohol thermometer.

With this apparatus some surprising results are obtained.

Not only the gases hydrochloric acid, hydrobromic acid, hydroiodic acid, silicium fluoride, arsenurate and phosphate of hydrogen, olefiant gas, which had been refractory till then, were easily liquefied, but the major proportions of the gases experimented with were even congealed. Hydrosulphuric acid takes the form of a white crystalline mass resembling camphor; protoxide of nitrogen that of a beautiful crystalline colourless body; hypochloric acid that of a friable red crystalline mass, etc. This is the confirmation almost word for word and indisputable of Lavoisier's beautiful conception.

Nevertheless, notwithstanding his attempts, Faraday remained powerless in respect to the very gases which had provoked them; five among them, hydrogen, nitrogen, oxygen, carbonic oxide and methane, withstood without turning a hair the most violent of his efforts, in the course of which he administered simultaneously 50 atmospheres and  $-110^{\circ}\text{C}$ .

## CHAPTER II

### THE CRITICAL POINT

#### NEW DIFFICULTIES: THEIR REASON BECOMES APPARENT.

FARADAY's set-back was, for physicists, almost a challenge. They applied themselves to take it up. Already in 1828 Colladon had compressed air to 400 atmospheres at  $-30^{\circ}\text{C}$ . in an apparatus which resembled, closely that which Cailletet was to use later. In 1838 Maugham was working on hydrogen and oxygen, which the electrolysis of water produced of itself under progressively increasing pressure. This ingenious arrangement did not actually give any results, but its author gave utterance to the reflection, remarkable at that period, that a sufficiently low temperature would, doubtless, facilitate success.

In 1843, Aimé, by utilising the extreme pressures which obtain at the bottom of the sea, had compressed without any greater success, oxygen and hydrogen to 220 atmospheres, produced by their immersion to over 2 kilometres in depth.

New efforts were thereupon made, but all with the unfortunate circumstance of over-estimating the importance of pressure, and not attaching sufficient to the lowering of temperature.

In 1850 Berthelot succeeded in acting with enormous pressures by means of a most ingenious and elegant device.

The gas under experiment was placed in the barrel of a simple thermometer, and the heating of the bulb caused the rising of the mercury, which subjected in this way, the



gas to an increasing and finally enormous pressure. Oxygen was thus subjected to 780 atmospheres, but not the smallest token of liquefaction could be observed, even when the tube was cooled by solid carbonic acid.

In 1854 Natterer made a new record in the scale of pressures by attaining the prodigious amount of 2800 atmospheres. Under these enormous pressures, reduced to a minute fraction of their volume, the gases experimented with proved heroically obstinate, they attained densities greater than that of water, but they did not capitulate! Thereupon these obstinate unconquered gases of Faraday were baptised. They were thereafter called *permanent* gases.

Brazen impudence, which science—which brooks not being defied—was not long in requiting, in the way we all know.

These obstinate gases were three simple bodies: Hydrogen, nitrogen, and oxygen, and two carbon compounds, carbon monoxide (CO) and methane (CH<sup>4</sup>). Moisson, by a celebrated investigation, added thereto in 1886, fluorine. Since then the list has been increased by a remarkable simple body, *helium*, which, through a strange paradox, our scientific men looked for and found in the sun before perceiving its presence on our globe, which the admirable work of Ramsay and Soddy has shown to be one of the most ordinary products of the transformation of the marvellous radium.

They could have added all those new elements, neon, argon, krypton, xenon, which we have thought well to discover in recent times in our atmosphere in company with helium, and which, according to Ramsay's latest work, are, doubtless, its brothers; one *could have*, we have stated, if unfortunately for our conceit these new-comers had not been revealed at a very dangerous time for the well-being of the *permanent* gases.

For, be it understood, we are manipulating these pretended permanent gases to-day by litres and tens of litres in the liquid form without many more precautions than if they were water or alcohol. One only of the lot, helium, has successfully defied down to the most recent times our means of coercion; but, being still a new-comer in the circle of our acquaintance, since its presence on our globe was only proved in 1894, it did not have a lengthy leisure to stick in its corner alone, for it only escaped the grasp of Dewar and of Olszewski to come to heel on the 10th of July, 1908, at the call of Professor Kamerlingh-Onnes.\*

In the event, on the other hand, the assertion of the scientific men who had formulated the qualification against which we have just been protesting, was all the less justified, seeing that experiments like those of Aimé and Natterer, among others, do not appear to have been happily inspired.

Seeing that the enormous cold, brought into play by Faraday, had remained impotent, in combination with very respectable pressures, it was hardly to be expected, we should think, that a better result could be obtained by the aid of pressure alone or combined with slight refrigeration. If anyone was well qualified to attempt the experiment of the use of high pressures, with some hope of success, it was certainly Faraday. Now, if he held it unnecessary to go in his experiments beyond 50 atmospheres, it was certainly not from inability, but because with a surprising clearness of vision he had very wisely saved himself from efforts which he knew would be fruitless.

**The Work of Cagniard de la Tour and Faraday's opinion.**—In fact, experiments carried out in 1821 by the French scientist, Cagniard de la Tour, which passed almost without attention in France itself, did not escape the genius of Faraday, who did not take long to find in them the

\* 'Proceedings of the Academy of Sciences,' August 17th, 1908.

reason of his own failure. By heating different liquids in closed vessels, which he almost completely filled, Cagniard de la Tour had seen these liquids at a certain temperature suddenly turn to gases without sensible change of volume, and consequently under very great pressures.

“At such temperatures,” wrote Faraday, “it is reasonable that no increase of pressure, unless it be enormous, could liquefy the gases thus formed. Now the temperature of  $-110^{\circ}$  is probably with hydrogen, nitrogen and oxygen above this degree, and, therefore, we ought not to expect that any pressure, except that which might accompany a cold, much more intense than any which has been able to be produced, could make them quit their gaseous condition.”

Berthelot, after the failure of his attempts, spoke in the same sense, and the celebrated experiments of Andrews were going shortly to demonstrate the perfect accuracy of these ideas. The degree of temperature below which, according to Faraday, it would be impossible to liquefy a given gas whatever be the pressure employed, exists very really; it is the *critical temperature*.

From Faraday to Andrews, however—that is, from 1845 to 1863—some interesting work still lightened the way.

Drion, who had already in 1845 re-discovered Cagniard de la Tour's results, but this time in connection with certain liquefied gases, remarked in 1859 that the dilatability of liquids increases rapidly where they are heated under pressure, and becomes comparable to that of gases when that strange stage is reached where the fluid passes indifferently from the liquid to the gaseous state. Here is evidently, taken in the raw, a manifestation of the progressive transition from the liquid to the gaseous state.

Mendeleeff, in 1861, made another very important remark: he determined that under these same circumstances the heat of evaporation of the liquid (p. 7) pro-

gressively diminishes, to be sensibly done away with, at the temperature of sudden gassification, which he also dubs the *point of absolute ebullition*.

Mendeleeff's observation explains that in this region a fluid takes on indifferently the liquid state or the gaseous state with very slight variations of temperature. This is an additional proof of the progressive transition from the liquid to the gaseous state. And in this wise we arrive at the year 1863 and the first work of Andrews.

**Andrews' experiments.**—This remarkable scientific man set forth by attacking the permanent gases and submitting them to the simultaneous action of pressures capable of attaining several hundreds of atmospheres and of temperatures lying between  $-75^{\circ}\text{C}$ . and  $-110^{\circ}\text{C}$ .

Like Faraday he failed; it was therefore in vain, in spite of the corrective element of temperature, which was already very low, that he should have also travelled along the road of high pressures. The views of his illustrious fellow-countryman thus received a new and important confirmation.

In despair of success, the experimenter thereupon very wisely turned his attention to a simpler problem, that of the liquefaction of carbonic acid, with a view to investigating its various circumstances. From this investigation, very modest in appearance, was destined to be born, six years later, the general theory of liquefaction, and the ideas more than ever prevalent at the present time on the continuity of the liquid and gaseous states. From the very first observations made by Andrews some interesting facts were brought to light.

Some carbonic acid is partially liquefied by pressure, so as to divide it into a liquid and a gaseous portion; then the whole is heated to  $31^{\circ}\text{C}$ . At this temperature all differentiation of the liquid level, all appearance even of the liquid vanishes. All the space is then occupied by a homo-

geneous fluid, but when the pressure or the temperature are slightly diminished, streaks appear throughout the whole fluid mass. Beyond this temperature where the fluid takes on indifferently the liquid or the gaseous temperature Andrews found *that no pressure* is any longer capable of liquefying the gas.

• Thus beyond  $31^{\circ}\text{C}$ . carbonic acid behaves like a true *permanent* gas. What can be more probable, therefore,

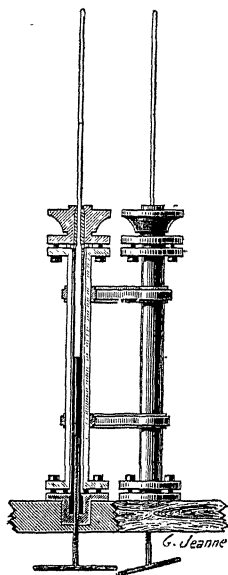


FIG. 19.

than that with permanent gases themselves, when acting in this way, their refractory behaviour is only a question of temperature!

Encouraged by these first results, Andrews undertook a more methodical and complete study of the phenomenon, and to this end devised the following apparatus (Fig. 19).

A tube *T*, carefully calibrated, is cemented in a metal cylinder *A*, furnished with a matrix in which a screw *v* works made perfectly tight by a stuffing box. The tube and

part of the cylinder hold some gaseous carbonic acid; the remainder of the cylinder holds the mercury destined to act as a piston on the gas and press it little by little into the calibrated tube when the screw *v* is turned so as to penetrate into the cylinder *A*. Another apparatus 'A'V', containing mercury and air is connected with the first below the level of the mercury through the tube *k*. The carbonic acid and the air are thus submitted at each instant to equal pressure, and as the air under the conditions of the experiment follows Mariotte's law fairly accurately, the tube *r* is only a compressed air pressure gauge indicating at each instant the pressure which is acting.

The results of these experiments are represented by the curves on Fig. 20, drawn by representing the volumes of the carbonic acid mass as abscissæ and the corresponding pressures as ordinates. Each of the curves *i*, *ii*, *iii*, *iv* and *v* of this figure relates to a series of experiments made at a constant temperature.

Working at first at pretty low temperatures Andrews checked the results obtained by preceding experimenters.

At 13° C., for example, the volume diminishes uniformly under the influence of pressure up to the moment where this reaches 50 atmospheres. This is the portion *ab* of the curve. A first drop of liquid appears at this moment. The screw *v* continues to force it way in and the volume to diminish. The liquid increases progressively till entire liquefaction takes place. Andrews observed that the pressure remained *constant*, and we know quite well that this must be so, since the pressure to produce liquefaction must only overcome the tension of the carbonic acid, which is quite determined and constant at the temperature of the experiment. Andrews noted, however, a slight increase of 1.5 atmospheres between the beginning and the end of the liquefaction, but this anomaly must be attributed to a trace of air in the carbonic acid, which, as we shall see

when dealing with the liquefaction of gaseous mixtures (Chap. XVI) must act in this direction.

This phase of liquefaction is represented on curve I

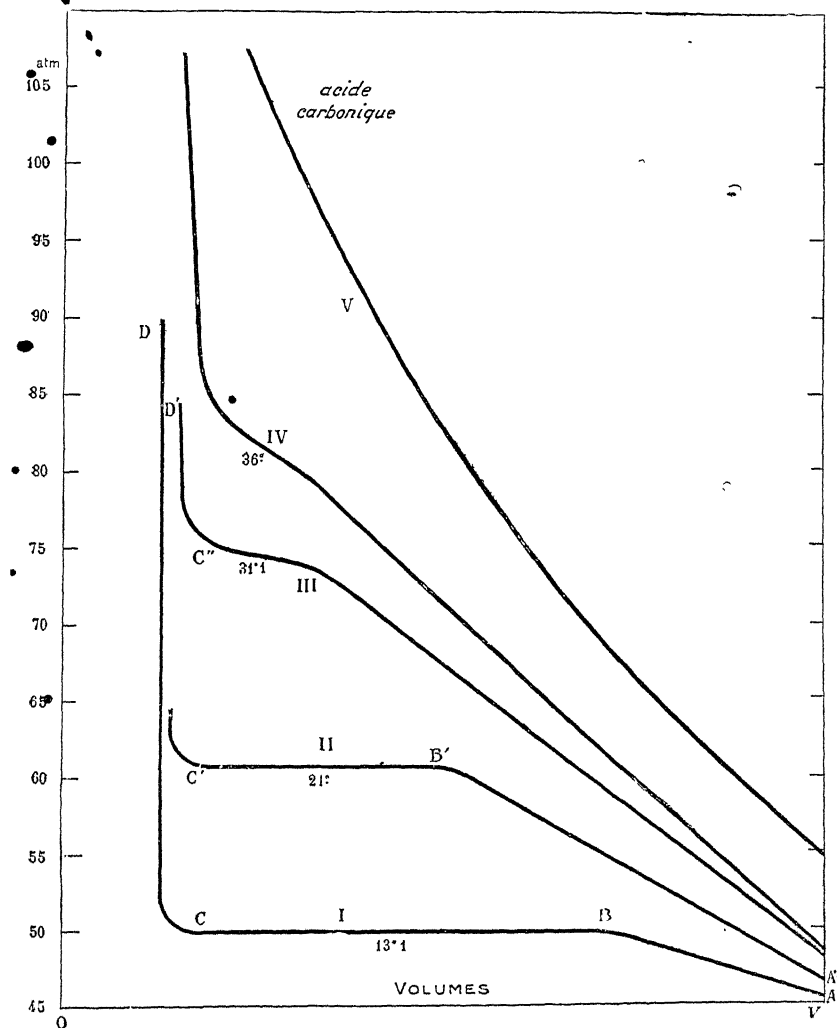


FIG. 20.—Andrews' curves for carbonic acid.

by the portion BC, parallel to the co-ordinate of the abscissæ, which clearly shows that during this period the volume diminishes without the pressure increasing.

At 50 atmospheres (about), always at the same temperature of  $13.1^{\circ}\text{C}$ ., all the gas is thus liquefied: thereafter very great increases in the pressure will not diminish the volume save very slightly, the liquid being at that temperature very slightly compressible; this is the portion *cd*.

At  $21^{\circ}\text{C}$ . (ii, Fig. 20), the phenomenon preserves the same conduct. We note only that the portion *cd'* is more developed than *ab*, and the pressure must attain a higher value—about 60 atmospheres—before liquefaction can commence. As in the previous case, this experiment is conducted entirely under constant pressure, but we find that the volume at the end of liquefaction represented by the abscissa at *d'* is greater than at  $13.1^{\circ}\text{C}$ ., which is not surprising, seeing that the liquid is hotter. At  $25^{\circ}$  and  $30^{\circ}$  the same occurs; the whole of the gas is always brought to the liquid state, but by means of higher and higher pressures. Besides this, the *horizontal* portion and the rising grade *bc*, which are very important features in the curves for  $13.1^{\circ}\text{C}$ . and  $21.5^{\circ}\text{C}$ ., are restricted more and more, and reduced to hardly anything at  $30^{\circ}\text{C}$ .; this signifies that at this temperature the reduction in volume at the moment of liquefaction is almost nothing, quite the contrary to what occurred at  $13.1^{\circ}\text{C}$ ., for example, and that therefore the gas, at the moment of liquefaction, possesses almost the same density as the liquid into which it is being transformed.

Manifestly, and notwithstanding that the liquefaction is still very apparent, an abnormal fact is imminent.

And if, in point of fact, we undertake at  $31.1^{\circ}\text{C}$ . a new series of experiments (curve iii), the phenomenon completely changes character.

Whatever the pressure which is attained it is impossible to discern a single drop of liquid appearing. If we construct with the experimental data a new curve (curve iii), we find for the angular type *ABC* of the low temperature



curves an almost continuous curvature is substituted. This curvature is such that at about 75 atmospheres the curve becomes almost horizontal, that is, that thereabouts all diminution of volume entails doubtless an increase of pressure, but that at least this increase of pressure is slight. Thus, we have here almost all the characteristics of liquefaction, condensation is immanent, so to say, and we have reason to hope that it is going to take place. False alarm, however, for this region of high compressibility is quickly passed, and, judging from the look of the curve *c''d''*, which continues its development, and which rises thereafter almost parallel to the co-ordinate of pressure, we note that all hope of liquefaction must be abandoned, and that it would be waste of time to try with this object in view still higher pressures.

#### THE CRITICAL POINT: CONDITIONS WHICH DETERMINE IT.

In this way, therefore, at  $30^{\circ}$  C., the gas in question is entirely liquefiable; while at  $31.1^{\circ}$  it is absolutely refractory to all our efforts. The reason is that between these two points it has crossed the limit, on which Andrews has quite appropriately conferred, the name of *critical point*, and which for carbonic acid corresponds to the temperature of  $30.9^{\circ}$  C. Let us make at this same temperature of  $30.9^{\circ}$  C. a new series of determinations with Andrews' apparatus. We shall find once more, but on this occasion for a body clearly classed as a gas, all the tokens of the phenomenon elsewhere observed in the case of liquids by Cagniard de la Tour. The pressure of the carbonic acid having been brought to 70 atmospheres, we notice that the gas, which has contracted very powerfully, can indifferently, owing to very slight variations of pressure or of temperature, pass wholly and at one stroke from the liquid to the gaseous state. As to the curve representing the phenomenon, its horizontal part *bc*, whose extreme reduction at  $30^{\circ}$  C., we have

pointed out, still exists here, but is reduced to a *single point*, which is a point of inflection, and which corresponds to the *critical volume*. At the critical point, therefore, the tangent of the curve is horizontal and it cuts the curve; it results from this that the critical point is determined by the two relations which mathematically define a tangent of this kind:

$$\frac{dp}{dv} = 0, \text{ and } \frac{d^2p}{dv^2} = 0.$$

We shall see (Chap. V) the remarkable use which Van der Waals has made of this property.

We thus see all the very remarkable conditions which define the critical point of carbonic acid.

First, it is the temperature below which it is impossible to liquefy by pressure alone, however enormous this pressure may be.

Then, at this temperature, the fluid passes without *change of volume* from the gaseous to the liquid state or *vice versâ*, and possesses consequently the *same density* in the gaseous as in the liquid condition.

Finally, and on this occasion Andrews confirms the results announced by Mendeleeff (p. 43), the indifference between the gaseous and the liquid state is explained by the fact that the heat of volatilisation, progressively diminished during the increase of temperature, disappears at the *critical point*, which demonstrates the progressive attenuation, and then the disappearance of the cohesion of the liquid.

#### CLASSIFICATION OF GASES FROM THE POINT OF VIEW OF LIQUEFACTION.

However remarkable the conclusions of Andrews may have been, they were only applicable till more ample information to carbonic acid alone.

Andrews himself undertook to underline their scope

by demonstrating that they were equally applicable to nitric oxide and methyl chloride.

Thenceforward, Cagniard de la Tour's experiments helped; it became indefinitely probable that all gases were subject thereto, and that therein lay most probably in accordance with Faraday's prevision the secret of the liquefaction of "permanent" gases.

Events, we have already stated, undertook to justify these ideas.

It results therefrom that gases from the point of view of their liquefaction can be classed under two categories :

(1) Gases characterised by critical temperatures *above* the normal temperature of our climates, such as carbonic acid, which has its critical point at  $31^{\circ}\text{C.}$ , acetylene at  $37^{\circ}\text{C.}$ ; chlorine at  $140^{\circ}\text{C.}$ ; sulphurous acid at  $155^{\circ}$ , etc. These gases, under ordinary conditions, find themselves automatically *below* their critical temperature, and it is not astonishing, therefore, that from the very first the physicists of the last century—Faraday, Thilorier, etc.—should have had the satisfaction of seeing these gases liquefied by the application of a sufficient pressure alone.

(2) Gases characterised by critical temperatures inferior to the ordinary temperature of our climates. These gases, under ordinary conditions, find themselves automatically above their critical temperature. The action of pressure alone will therefore always be powerless to bring them to the liquid state, and to succeed in doing so, it will be necessary by means of rather energetic cooling, to bring them first below their critical temperature. The gases prematurely dubbed as "permanent" pertain naturally to this category. They are characterised by critical temperatures which are *fearfully low*, temperatures of which we had no idea till the last dozen years.

It is thus, if we put oxygen on one side, whose critical temperature of  $-118^{\circ}\text{C.}$ , is barely below the  $-110^{\circ}\text{C.}$ ,

which Faraday worked with, that carbonic oxide has its critical point at  $-136^{\circ}\text{C}$ ., nitrogen at  $-146^{\circ}\text{C}$ ., and that hydrogen, the one which reaches the fantastic degree of  $-242^{\circ}\text{C}$ ., so close to that extreme temperature  $-273^{\circ}\text{C}$ ., which physicists, guided by wide conceptions, considered to be the extreme limit of temperature possible, and which they consequently styled the *absolute zero*. Thus, the necessity for cooling of extraordinary intensity is explained, to compass the liquefaction of these gases, and the repeated set-backs of physicists who pinned their best hopes upon the indefinite increase of pressure, are easily understood. It is even worth noting in this connection that as soon as they are cooled down to their critical temperature the permanent gases allow themselves to be liquified invariably under moderate pressures—33 atmospheres for nitrogen, 50 for oxygen, 15 for hydrogen; and still less if the cooling is carried below the critical temperature. As in all other cases the difficulty is to know how to tackle it, and the enormous pressures which the physicists of the last century made use of, at every turn, are perfectly superfluous.

It will be remarked that this classification of the gases in one or the other of the two categories is based entirely upon the average temperature which the present conditions of the solar system impose upon our globe.

If we unfortunate mortals were living upon one of those glacial spheres which are wandering near the limits of our system, and where temperatures of  $-200^{\circ}\text{C}$ . to  $-250^{\circ}\text{C}$ . prevail, we should have been spared the singular idea of dubbing oxygen and nitrogen as permanent gases, since they would be running as liquids in our streams, or would form, according to Lavoisier's dictum, solid mountains or very hard rocks. While hydrogen and helium alone, yielding to the blandishments of physicists, would have been coquettish enough to wait upon the perseverance of an Andrews or the ingenuity of a Cailletet.

**Andrews' classification.**—It should be noted that Andrews, struck by the extreme importance of this circumstance of the critical temperature of gases, proposed a very logical classification of gases and vapours. In his opinion gases properly so-called are fluids under such conditions of temperature that it is impossible for them to pass into the liquid state under the influence of pressure; they are fluids *above* their critical temperature. Vapours, on the contrary, are fluids capable of passing to the liquid state under the influence of pressure alone, or, in other words, are fluids *under* their critical temperature.

By Andrews' definitions, therefore, the only real gases are the permanent gases. All the rest would be only vapours.

However logical this definition may be, we could not adopt it, because it would have the drawback of outraging without profit our habitual ideas, by classing among vapours the greater number of bodies which we consider as gases, carbonic acid, sulphurous acid, etc., so we shall preserve as very logical also, the definition that we have adopted above (p. 24), and which consists in considering as synonymous the terms *gas* and *non-saturated vapours*. As to the term "permanent gases," we shall continue using it as a convenient locution, but without having any illusions as to its applicability.

## CHAPTER III

### THE LIQUEFACTION OF THE PERMANENT GASES

**Cailletet's experiments.**—After Andrews' work the goal appeared to be close. Nevertheless, another eighteen years elapsed without appreciable progress. But on Monday, December 24th, 1877, a circumstance occurred almost without precedent in the history of science. The French Academy of Sciences, who met on that date, was informed that the grand problem of the liquefaction of the permanent gases, a problem which for so long had been the subject of investigation, for the solution of which so many fruitless efforts had been made, was at last solved, and solved in no vague and uncertain manner, but by two experimentalists unknown to each other, by means of two completely distinct methods. One of these experimentalists was the French scientist Louis Cailletet, son of an ironmaster of Chatillon-sur-Seine, who had already become known through his many investigations connected with the problems that the working of blast furnaces were raising day by day, when he turned his attention to the liquefaction of gases.

Cailletet commenced by arranging a convenient apparatus for his experiments. It happened that this apparatus was almost identical with that of Andrews, and an arrangement Colladon had used fifty years earlier for the researches to which we have alluded (p. 40).

Some mercury contained in a block of steel A (p. 56), arranged so as to be pumped by a hydraulic press into the glass reservoir T containing the gas under experiment,

and terminated outside the block of steel by a chamber of smaller diameter. When the pressure reaches a sufficient amount, the gas is forced by the mercury into the upper part of this reservoir  $\tau$  which only is subjected to high pressure, a condition which is easily fulfilled because of its small internal section. Thanks to the volume of the recipient it is possible in this way to act on a considerable mass of the gas, and the whole of the interesting phase occur under the eyes of the experimenter.

Now, it was by the aid of this very simple apparatus that out of the five "permanent" gases then known, four have been able to be finally deprived of this absurd qualification, and that hydrogen itself presented unequivocal traces of liquefaction! Apart from its enormous scientific interest, the matter did not lack its piquant side.

We have just seen that Andrews' work had indicated the road for physicists; that to finally succeed in liquefying the permanent gases, the only hope, in the words of Faraday, lay in subjecting them to a cold more intense than any which we had then been able to produce. And it happened that in the apparatus itself, with the help of which human science was going to win this decisive victory, nothing was provided to apply an intense refrigeration to the gases under experiment, since the mercury, which is liable to being easily congealed, was in direct contact with the gas under experiment.

It will be sufficient for us to add, to explain this extraordinary conception, that Cailletet by no means had in view Andrews' experiments, but that at the outset of the experiments which he intended to be of very modest scope he did not expect to deal with the permanent gases.

One of his *objects* was to easily repeat successive experiments with the same mass of gas. He intended to this end to furnish his apparatus with a valve  $v$ , with which he could evacuate the water used in the hydraulic press,

and consequently do away with the pressure and return the gas to its original condition; the instrument was ingeniously designed, but its results were destined to singularly surpass the hopes of its author.

Thus equipped, Cailletet commenced his investigations. Acetylene was the first to be experimented on. This remarkable gas, discovered in 1836 by E. Davy, and studied by

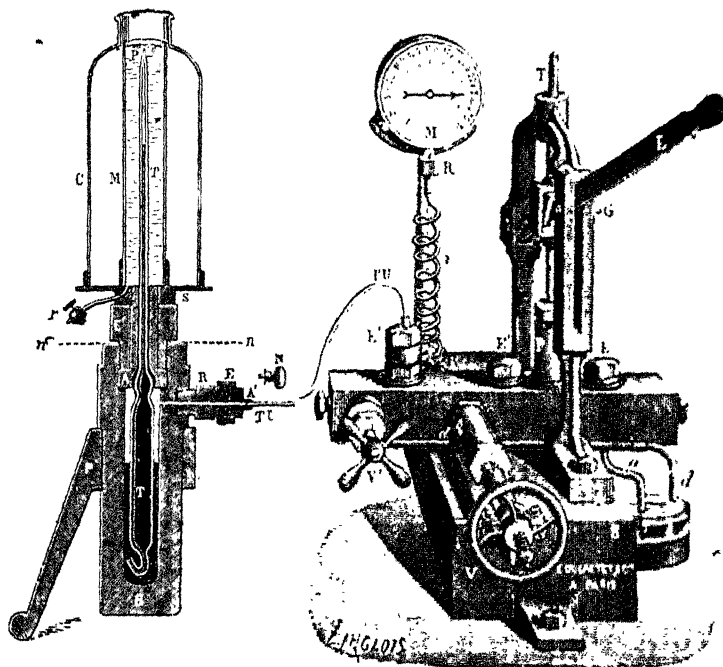


FIG. 21.—Cailletet's apparatus.

Berthelot, who produced a masterful synthesis thereof, cannot be claimed to be very refractory to liquefaction, as its critical temperature is at  $37^{\circ}\text{C}$ . At this temperature 68 atmospheres are sufficient to liquefy it. It was therefore for Cailletet rather a verification than a serious experiment.

Now, in the course of the verification, an incident occurred which was destined to decide the success of the play. During an experiment, when the pressure had not



attained the amount sufficient for liquefying the gas, the discharge valve was opened by accident; the operator saw at this moment the contents of the tube becoming upset and taking on the appearance of a thick mist.

Cailletet himself was not upset; he did not at all realise that he had witnessed a very important fact, for, in his opinion, the mist he had observed arose from a simple condensation of the moisture or the impurities contained in the gas. A superficial experimenter would have been content with this explanation, and would have passed without delay to another experiment. How often this occurs in scientific experiments! How often has an ingenious explanation—and what can we not explain by exciting our imagination—causes us to pass over a strange phenomenon which we have observed on the way and miss some great discovery thereby!

Cailletet, however, decided that he was not satisfied with the explanation till he had verified its exactitude. Since it was the impurities which were the culprits, he decided to procure some absolutely pure and dry acetylene, and to ascertain that in this case the phenomenon which had attracted his attention, would not repeat itself. The laboratory of Berthelot furnished him with the required gas, the experiment was repeated, and the mist reappeared still equally intense.

A new experiment was carried out with protoxide of nitrogen, with the same result: this was becoming serious. Cailletet was obliged to be persuaded that he was the witness of a veritable liquefaction.

He concluded thereupon, that this must be the manifestation of a fact well known in thermodynamics, but which he had not the slightest idea would intervene in such an experiment.

In fact, the *sudden* expansion to which the gas was subjected at the moment of opening the valve must have

been the cause of a theoretically very intense cooling, but which it was possible to calculate long ago in thermodynamics by Laplace's formula. But how was it possible to suppose that such a cooling could be effectively obtained in the interior of an almost capillary tube, with such a small mass of gas, subjected on all sides to the heating effect of the tube walls?

This victorious intervention of chance was necessary to demonstrate, in the most peremptory fashion, that because of the excessive suddenness of the phenomenon and of the bad calorific conductivity of the gas, the influence of the walls was on the contrary negligible, and quite unable to bring the temperature up, in the centre of the tube to its own value save with delay of some seconds; quite sufficient to reveal to the operator all the secrets of the phenomenon.

We can now reconstitute what must have passed in Cailletet's mind.

Since such intense cooling seem to be very easily realised by this device, would it not be possible, by increasing the pressures and by acting no longer on the modest gases of the first category, but on the "permanent gases" themselves, to arrive in these cases also below the critical temperature? The apparatus without any change lent itself admirably to the application of pressures exceeding 300 atmospheres: the trial was tempting. It was carried out after some preliminary experiments in the case of methane on December 2nd, 1877.

The following letter, written to Sainte-Claire Deville, who had encouraged with his advice a beginner whom he loved, gives the results of this memorable experiment in terms whose very modesty and scientific reserve enhance the merit of the experimenter:

"I hasten to inform you, and you first without losing a moment, that I have liquefied this day both carbonic oxide and oxygen. I am, perhaps, wrong in saying liquefied,

because at the temperature I obtained by evaporating sulphurous acid, that is at  $-29^{\circ}\text{C}$ ., and under 200 atmospheres' pressure, I did not see any liquid, but a dust so dense that I was able to infer the presence of a vapour very close to its point of liquefaction.

"I have written to-day to Mr. Deleuil to ask him for some protoxide of nitrogen, by means of which I shall doubtless be able to see carbonic oxide and oxygen flow.

"P.S.—I have just carried out an experiment which satisfies me completely. I have compressed hydrogen to 300 atmospheres, and after cooling down to  $-28^{\circ}\text{C}$ ., I expanded it suddenly. There was no trace of liquid dust in the tube. My gases (CO and O) are therefore certainly at the point of liquefaction, as this dust is only produced by vapours close to liquefaction. The forecasts of M. Berthelot are completely verified."

The result in respect to oxygen was not surprising, because the cooling, calculated by Laplace's formula with a pressure of 300 atmospheres, could not have been less than  $220^{\circ}\text{C}$ .!

The experiment, however, was not made public neither at the sitting of the Academy of December 3rd, nor at that of the 10th, nor at that of the 17th. What did this reserve mean, corresponding so little with the intense satisfaction which the happy experimenter could not help feeling? The explanation is to be found in a circumstance wholly to his honour. Cailletet, whose brilliant work, we have said, had already attracted the attention of the scientific world, had become a candidate for a corresponding membership of the Academy; the election was to take place on the 17th December, and he did not wish to appear to have influenced the voting by such a sensational communication.

He was elected, but this exaggerated modesty nearly cost him dear. It is the rule, in fact, in France, that questions of priority should be settled by the dates of

presentation to the Academy of Sciences. Now, the last evening but one before the 24th December, the day on which Dumas was to have presented to the Academy the discovery of their new correspondent, a dispatch reached the Institute. It announced that on that very day, the 22nd of December, oxygen had been liquefied, and it was signed, Raoul Pictet!

Happily for Cailletet, Sainte-Claire Deville, an old *habitué* of the Institute, had mistrusted possible indiscretions; he had taken on himself to lodge in a sealed envelope with the Academy the historical letter, the text of which we have quoted, and by his foresight he had definitely assured for his *protégé* the priority which had almost been taken from him.

The experiment of December the 2nd naturally was not only repeated successfully with enormous success before a number of enthusiastic scientists, but it was applied to the different gases which remained to be liquefied. Methane, nitrogen, air all behaved in the same abject fashion as oxygen. The inconclusive experiment mentioned in Cailletet's letter relating to hydrogen was repeated, starting from 300 atmospheres and from  $-28^{\circ}\text{C}$ ., before a committee of the Academy composed of Berthelot, Sainte-Claire Deville, and Mascart, disclosed also a commencement of indubitable liquefaction by the appearance of an "excessively *fine and tenuous* mist, which filled the tube and suddenly disappeared." Now, to realise the extreme power of the method which furnished these results, it will suffice to recall that the critical point of hydrogen is no less than  $-242^{\circ}\text{C}$ .

Unfortunately, though the success of this magnificent experiment from the scientific point of view was complete, we have seen that it was not equally so from the practical point of view, since the tricky mists of Cailletet's apparatus only appeared, to at once disappear.

**Pictet's experiments.** — Pictet, the ingenious Geneva physicist, had arrived at the goal by an entirely different route, equally very interesting and more directly inspired by Andrews' work. We know that in accordance with Faraday and with Andrews, the permanent gases might not be liquefied save on condition of submitting them, at the same time as to pressure, to a sufficient degree of cold. All the efforts of experimentalists should therefore have been turned to producing this cold. Now, the principle brought into play to this end by Pictet consists in cooling, by means of *cascades* or *successive falls*, of more and more refractory liquefied gases, *each term* of which, by reason of having its boiling-point lower, *permitted of the liquefaction of the following term without too much trouble*.

Pictet, in the event, was utilising the idea put forward ten years earlier by a scientist of more than average ingenuity, the real creator of the refrigerating industry which is so flourishing at the present time, the Frenchman, Ch. Tellier.

In a remarkable work\* full of manufacturing suggestions, many of which could be taken up again now with advantage, Ch. Tellier enunciated the principle which interests us, in connection with a very curious application, otherwise far removed from the sphere of the ideas which occupy us, and which was required in connection with the manufacture of great quantities of liquid carbonic acid.

Anxious not to find in their manufacture the necessity for the enormous pressures, which the bursting of a Thilorier apparatus and the death of the unfortunate Hervey had shown to be dangerous, Tellier proposed to liquefy the carbonic acid in a bath of boiling ammonia under reduced pressure. The condensation of the carbonic

\* 'L'Autonomique,' by Ch. Tellier, published by J. Rothschild, Paris, 1867, p. 277.

acid was thus brought about under 7 atmospheres, and all serious danger was also avoided.

In his experiments on the liquefaction of air, Pictet replaced the ammonia recommended by Tellier by sulphurous acid, with which his experience in the manufacture of ice machines had familiarised him.

This liquid, produced by compression under 3 atmospheres, was caused to boil under reduced pressure, and to develop a temperature of  $-65^{\circ}\text{C}$ ., around a system of tubes in which carbonic acid was being condensed under feeble pressure. This liquid carbonic acid was in its turn taken up and transmitted to boil under reduced pressure in a second recipient, where it developed—according to the author—a temperature of  $-130^{\circ}\text{C}$ ., and where it finally brought about the liquefaction of oxygen produced directly under a pressure over 200 atmospheres by red hot decomposition of chlorate of potash in a steel shell. By opening the needle valve which closed the portion of the oxygen holder which is plunged into the carbonic acid, Pictet observed this body escaping under the form of a transparent jet surrounded by a concentric white cylinder, which he took for solid oxygen.

From this beautiful experiment he thought he could conclude that the vapour tension of oxygen at  $-130^{\circ}\text{C}$ . was about 273 atmospheres. In the course of subsequent experiments Pictet did not hesitate to attack hydrogen, which he also prepared under pressure, in a similar fashion to Faraday, by the action of potash or formiate of potash. Pictet, influenced doubtless by the inductions of chemistry, which tended at that time to consider hydrogen as a metal, thought he saw it issuing from his apparatus in the form of an opaque jet, with a very characteristic tint of *steel blue*, which struck the ground with a noise recalling that of metallic shot.

It would be evidently unjust to contest Pictet's very

great merit in these superb experiments, and the very great experimental ability which enabled him to bring them to a happy issue. "Unfortunately," says Julius Lefèvre,\* "it was found a few years later that Pictet's results were contaminated by serious errors. Subsequent experiments have demonstrated that oxygen can be liquefied at  $-130^{\circ}\text{C}$ . under a pressure of about 25 atmospheres, while hydrogen, whose critical temperature is well under

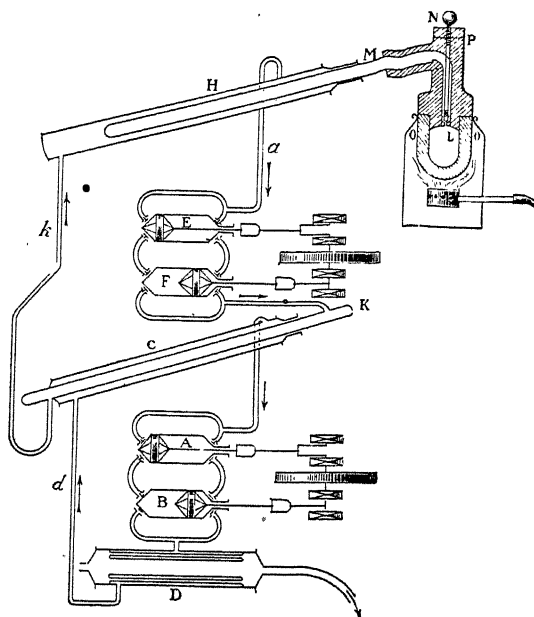


FIG. 22.—Pictet's apparatus.

$-200^{\circ}\text{C}$ . could neither be liquefied nor solidified in a tube at  $-140^{\circ}\text{C}$ ., as Pictet believed he had observed, and that if liquefaction did occur it could only be produced outside the apparatus under the influence of expansion."

On the other hand, it would have been a further error on Pictet's part to believe that the reaction he used in his second series of experiments could furnish him with pure

\* 'The Liquefaction of Gas and its Applications,' by J. Lefèvre, published by Masson, Paris.

hydrogen, when in point of fact he was rather copiously adulterating it with water and carbonic oxide.

Lastly, while the author asserts in definite terms that he also saw a blue substance liquid hydrogen, this, according to our present knowledge, is a colourless liquid, extraordinarily light and very mobile!

Science could not therefore rest contented with numerical determinations furnished by Pictet's undoubtedly very interesting but apparently too precipitate experiments.

On the other hand, as Jamin pointed out to the Academy on December 24th, 1877, the problem was not as yet entirely solved; it was still necessary to assemble under a more visible and more stable form the impalpable droplets seen by Cailletet and Pictet and arrive at the normal manipulation of the mysterious liquid.

"The possibility of liquefying or of solidifying oxygen is now demonstrated. The two experiments are as good as each other; Pictet's added little to Cailletet's, for if the first proclaimed that he had seen oxygen deposited in liquid form, everything tends to show that he only caught a flying look, and, on the other hand, the mist observed by Cailletet at the moment of expansion showed that the oxygen had ceased to be transparent—that is, gaseous—and that it had become solid or liquid. To have seen the liquid or the mist without being able to collect either one or the other showed that the crucial experiment had still to be made. It should consist of maintaining liquid oxygen at the temperature of its point of ebullition, as has been done in the case of the protoxide of nitrogen, or in the solid state as with carbonic acid, which is preserved in this condition because of the enormous latent heat which gassification exacts."

**Experiments of Olszewski and Wroblewski.**—Some much more careful experiments were thereupon undertaken by Cailletet himself.



About the same time two Polish scientists of the highest skill, Olszewski and Wroblewski, one of whom had been very deeply impressed by the memorable experiments which he witnessed in Cailletet's laboratory, setting to work at the University of Cracow, were able to fix the conditions of

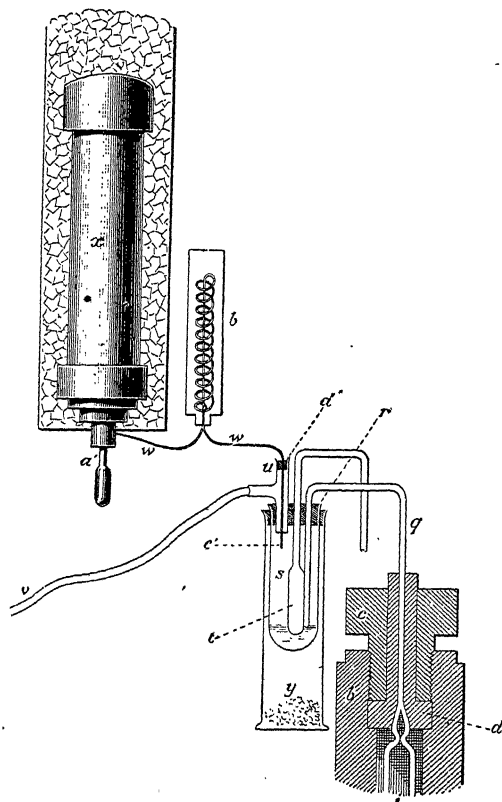


FIG. 23.—Apparatus of Wroblewski and Olszewski.

liquefaction and the physical constants of the permanent gases more exactly.

To arrive at the results established by Jamin, it sufficed for the two last experimentalists to arrange Cailletet's tube under a form (Fig. 23) permitting of subjecting the compressed gases to a more intense cooling. Wherefore to the reservoir a doubly curved tube is added, which plunges into

a refrigerating bath. Under this form the principle of the process is completely changed; expansion has nothing further to do with the matter. The apparatus as thus arranged is a descendant of Faraday's apparatus rather than anything else (p. 38). But the Polish experimenters owed their success to the fact, suggested by Cailletet, of having used as cooling agent, instead of solid carbonic acid, some liquid *ethylene*, whose ebullition *in vacuo* would secure a temperature of  $-136^{\circ}\text{C}$ . Notwithstanding the very low temperature which this body can yield, its critical temperature is only  $+9^{\circ}\text{C}$ ., and it can therefore be liquefied under moderate pressures in simple refrigerating mixtures or in sulphurous acid boiling under reduced pressure.

The measurement of the temperatures is ensured by a hydrogen thermometer, whose bulb is immersed in the refrigerating liquid, and thus permits of the temperatures being estimated by the contraction of the hydrogen—which, according to Gay Lussac's law, is equal to  $\frac{1}{273}$ rd part per degree—all the substances used for thermometers, in fact, such as alcohol, carbon disulphide, etc., would be instantly solidified at these temperatures, as stated by Wroblewski, who did not then know the properties of petroleum ether (p. 160). It has been proved, however, that hydrogen can be used without fear at these temperatures, because it is still far enough removed from liquefaction to follow very exactly Gay Lussac's law.

It is by means of this arrangement that the two Polish scientists have transformed into a definite victory the first success achieved by Cailletet over the hostility of matter.

On April 9th—1883—a memorable date—they saw oxygen, previously compressed to 20 atmospheres, assembling in small colourless drops at the lower side of the curved tube. What pains, what ingenuity, what difficulties overcome, were represented by these few droplets of liquid! but also what enthusiasm for the first experimenters,

so whom at length it had been given to see the fluid which we breathe transformed into an unruffled limpid liquid as similar to water as two drops of that fluid are to each other! The temperature of persistence of this liquid was found to be  $-129.6^{\circ}$  C. under the pressure of 27 atmospheres, and  $-135.8^{\circ}$  C. under 22.2 atmospheres.

The experimenters described the liquid they obtained as transparent and very mobile, presenting an apparent but fairly flat meniscus and finally colourless. It is in reality pale blue; but its colour was, doubtless, not observed during these first experiments, because of the small quantity which the experimenters had at their disposal.

Nitrogen and carbonic oxide could not be liquefied save at  $-136^{\circ}$  C., by simple compression, even with 150 atmospheres. In the case of nitrogen this is fairly reasonable, since we know to-day that its critical temperature is  $-146^{\circ}$  C. In the case of carbonic oxide its liquefaction was missed by an ace, since its critical point corresponds with  $-139^{\circ}$  C.

Moreover, the two Polish experimenters were not going to be satisfied with their want of success. By lowering slowly down to 50 atmospheres the initial pressure of 150 atmospheres, to which these gases were subjected, they saw them transformed completely by means of expansion into colourless liquids with clearly defined meniscus. But as soon as they became apparent, these liquids commenced to boil and quickly disappeared, because of the external temperature of  $-136^{\circ}$  C.

These two liquids could only have been maintained for a few seconds in the condition of statical liquids, and Lamin's programme, so far as it applied to them, had only been imperfectly followed when Wroblewski, in 1885, thought of a more perfect device. Thanks to recipients with multiple envelopes pervaded by the cold vapours of the

refrigerating liquid, a sort of very effective screen was realised preventing the penetration of the surrounding temperature; in this way the pressure of evaporation of ethylene can be lowered down to 1 cm. of mercury, and a temperature of  $-152^{\circ}\text{C}$ . obtained.

The critical temperatures and pressures were measured in this series of experiments, and they were respectively—

For nitrogen	. . .	$-146^{\circ}\text{C}$ . and 33 atmospheres.
For oxygen	. . .	$-118^{\circ}\text{C}$ . and 50 atmospheres.
For carbonic oxide	. . .	$-141^{\circ}\text{C}$ . and 35 atmospheres.

The nitrogen and carbonic oxide obtained in the condition of stable liquids and afterwards evaporated *in vacuo* became solid about  $-200^{\circ}\text{C}$ .; in fact, according to Travers, the temperature of solidification of nitrogen is  $-213^{\circ}\text{C}$ .

Oxygen itself has not been able to be solidified. We now know practically that its point of congelation is not yet attained at  $-225^{\circ}\text{C}$ . On his side Cailletet did not remain inactive. He succeeded about the same time as the two Polish scientists in attaining identical results in a possibly preferable manner, by applying in his turn the process of multiple cycles and liquefying methane under slight pressure with the aid of ethylene, which permitted him to attain some very sufficient temperatures, viz.  $-160^{\circ}$ , by simple ebullition in the free air. At the same epoch the English scientist Dewar, worthy successor of Faraday, was commencing at the Royal Institution a series of splendid researches which were destined to result in the most extraordinary results, of which we shall have to speak later.

**Experiments of Kamerlingh-Onnes.**—Finally, at the cryogenic Laboratory of Leyden, under the direction of Kamerlingh-Onnes, extensive experiments of the highest interest were undertaken concerning the action of low

temperatures on the properties of bodies. A machine was designed for the purpose which was only a perfected Pictet machine, in which the different stages of temperature were produced by methyl chloride, ethylene, and finally oxygen. In the first cycle liquefied methyl chloride was used, which by its evaporation in contact with ethylene furnished a temperature which could attain  $-70^{\circ}\text{C}$ . These vapours, sucked into a pump and compressed, reverted to the liquid state, in a condenser cooled by water, and the liquid thus reformed is returned to be evaporated in contact with ethylene so that the operation is continuous.

In the second cycle the evaporation at  $-60^{\circ}\text{C}$ . or  $70^{\circ}\text{C}$ . methyl chloride is utilised to take up the heat of liquefaction of the ethylene when compressed to several atmospheres.

The liquid ethylene serves in its turn, by being evaporated at  $-150^{\circ}\text{C}$ ., under the reduced pressure maintained by the pump, to absorb the latent heat of oxygen when being liquefied. The ethylene vapours, after being sent through an exchanger of temperatures (p. 75), are compressed by the pump, and passed through an exchanger in the contrary direction, being then delivered to the methyl chloride refrigerator, which reverts them to the liquid state; and so on.

Finally, the oxygen, cooled to  $-150^{\circ}\text{C}$ . by the ethylene, is liquefied quite easily under a few atmospheres pressure. The liquid oxygen thus produced is sent to be evaporated under reduced pressure into a part of the apparatus, where a temperature of  $-200^{\circ}\text{C}$ . then prevails. The vapours are taken up again through an exchanger, re-compressed, and re-passed through the exchanger in the contrary direction, and re-liquefied in contact with the ethylene, etc.

In this way an apparatus for investigation was produced which, though certainly complicated, placed in the hands of

the operator the whole gamut of low temperatures from  $-50^{\circ}\text{C.}$  to  $-200^{\circ}\text{C.}$ , and which Professor Kamerlingh-Onnes has completed in the last few years by the addition of a helium cycle which has brought its scope to within  $3^{\circ}\text{C.}$  of the absolute zero temperature!

We will, with this remarkable specimen of scientific technology, terminate this chapter of the history of the liquefaction of gases.

# PART II

## THE COMMERCIAL LIQUEFACTION OF AIR

### CHAPTER IV

#### EXPANSION AND SIEMENS' EXCHANGER OF TEMPERATURES—FROM SIEMENS TO LINDE

**Insufficiency of the multiple cycle process.**—Apart from the wonderful apparatus of Cailletet (p. 56), which only gave a fugitive glimpse of the liquefaction of gases, we have seen that the physicists of the last century founded their means of success on the principle of multiple cycles.

Now, notwithstanding the elegance of this process, notwithstanding the warm reception given by scientists to this powerful method of investigation, its complicated character and the cost of its application were certainly not of a character to open thereto the portals of practical manufacture.

But note here the very strange expression, "practical manufacture," in this connection!—commercial applications founded on these strange liquids which a long century of effort had barely taught men to produce by minute droplets! Well, yes, however impossible the matter might seem, like so many other unlikely things it has been realised, and the liquefaction of the permanent gases, that of air more particularly, is on the way to assuming a privi-

leged place among the important industries of to-morrow. An absorbing industry furthermore, since it possesses the happy characteristic of uniting the most indisputable scientific interest to an industrial scope whose unlimited horizon which we have been disclosing in the course of these pages hardly gives an idea.

To have rendered this unexpected development possible, it has evidently been necessary that the methods of liquefaction known up to that time, that this process of multiple-cycles which has been described a few lines above, should have given place to something of a much more practical kind. This something is to a very large extent the general application of *expansion*.

#### WHY DOES EXPANSION PRODUCE COLD ?

We have had occasion to remark, when speaking of Cailletet's apparatus (p. 57), that long ago, expansion has been recognised in connection with compressed gases to be an extremely powerful source of cold. Cailletet's method itself gives the best possible proof of its efficiency, since we have seen it capable of bringing hydrogen at a single stroke down to the extraordinary temperatures which attend about its liquefaction. Thus, this compression, which we already know as a condition which is itself favourable to liquefaction, is now presented to us under a second aspect, and is going to furnish us, with unparalleled simplicity, the source of cold which we require.

Here, in this connection (Fig. 24), is a small lecture-room experiment which allows us to descry, in spite of the modest means employed, the extreme power of the process. A flagon A, one third full of water, is stoppered by a cork with a hole in it through which is passed the stem of a rubber ball. By squeezing this, the air in the flagon is compressed. We wait a minute till the equilibrium of the pours given off by the liquid is re-established, then we



let the ball expand to its original volume so as to relieve the compressed air. Notwithstanding the small pressure involved, the cooling produced by the expansion causes the instantaneous formation, in the air space of A, of a very definite mist, due to the condensation of the moisture which it contained.

It is in miniature, Cailletet's experiment !

Now, by what mechanism does expansion produce cold ? When we compress air everybody knows—through having experienced it more or less in spite of themselves, when pumping up the tyres of a bicycle—that air thus com-



FIG. 24.—Demonstration of the frigorific effect of expansion.

pressed heats considerably. Thermodynamics teach us, moreover, that the quantity of heat which is evolved in this way is exactly equivalent to the work expended to effect the compression.\* Thus, when a gas is compressed it gets hot, because of the transformation of the mechanical work into heat, this should not astonish us since mechanical work and heat are two different forms of one and the same thing.

Inversely, when a gas expands, it *cools*, and if it gets cooler it is because it produces always during expansion a certain amount of work. Contrary to what occurred previously, we assist in this case at a transformation of heat into work, and the quantity of heat dissipated, or in other

\* This is not, as we shall see, rigorously exact for "real" gases.

words the quantity of *cold* produced, corresponds to the *work effected* by the compressed air during expansion. Hence the manifest conclusion that the greater the *work effected* by the compressed air during expansion, the more considerable its cooling will be.

### TWO PRINCIPAL METHODS OF EXPANSION.

To expand the compressed air, no longer in a *discontinuous* manner, as was the case in Cailletet's apparatus and in our little experiment alluded to above, but in a *continuous* manner, such as is required for a manufacturing installation, many different methods can be devised.

We could, for example, expand it by letting it simply flow out through a valve, between its initial and its final pressure. This is a very bad way of making the compressed air produce cold, because it is manifest that to make it do a maximum of work, it would be necessary to place an obstacle in the way of expansion, an obstacle which it would have to overcome to increase its volume.

Or, alternatively, we could arrange for the air to produce during expansion, all the work of which it was capable, by making it impinge on the vanes of a turbine, or actuate the piston of a machine analogous to a steam-engine running under a load; and it does not seem doubtful, that this method would be much better than the other, for our purpose. For example, we could draw off through a valve air compressed to 10 atmospheres, without anything apparently occurring; if we, on the contrary, allowed this air to expand in a small compressed-air motor (Fig. 25) working against an external resistance, break, generator, or such like, we should at once assist at a manifestation of cold of an extreme character; the motor, almost instantaneously, could be covered with frost, while the escaping air will issue under the appearance of a thick jet of smoke pro-

We shall be somewhat surprised after what has preceded to learn that the first process has been applied to the absolute exclusion of the second till the success of the author's own endeavours. This is really because between the precarious starting-point laid down above and the manufacturing application, there intervenes a whole chapter, one of the most remarkable, in applied physics—that of Professor Linde's work.

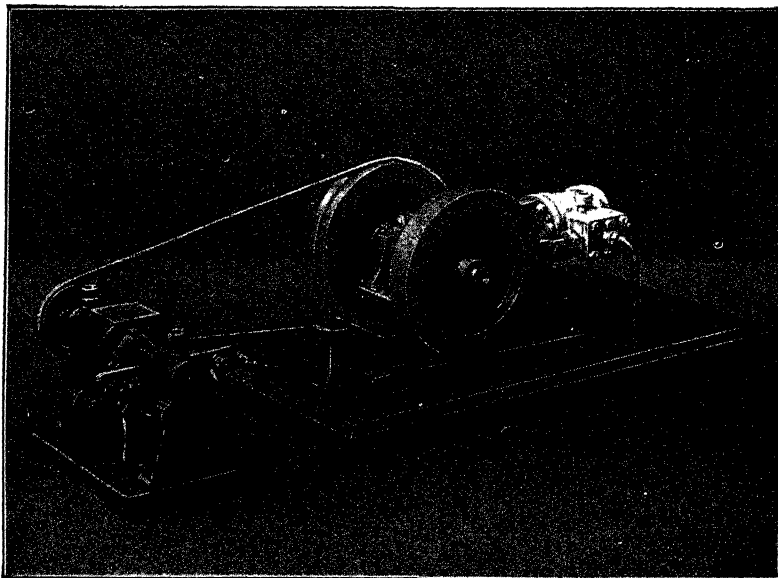


FIG. 25.—Production of cold by expansion of compressed air in a motor.

The two methods at the present day are currently applied in manufactures on about an equal scale.

#### **NECESSITY FOR EXCHANGERS OF TEMPERATURES.**

We shall return at some length a little further on to this capital question of the choice of methods of expansion, but, before anything else, it should be observed that to arrive directly and at one stroke by means of expansion at

the liquefaction of permanent gases, it would be necessary to compress these under enormous pressures, both very wasteful and very dangerous. Cailletet, in laboratory experiments, could venture to do this. In manufacturing it would not be permissible, all the more since only an infinitesimal portion of the gas expanded can be liquefied in this way.

On the contrary, if we limit ourselves to low pressures only, the lowering of temperature will be very limited, and will not lead very far along the road to the distant regions which have to be reached for liquefaction.

This dilemma seems embarrassing.

Happily, a precious device, thought of in 1857 by Siemens, allows us to amplify as much as we like the initial cooling furnished by the expansion. As much as we like, with the reservation that Siemen's conception, we must not forget takes us back to a period when—Faraday's ideas notwithstanding—the theory of permanent gases was completely unquestioned.

In reality, when following the letter of Siemen's programme, the operator is very quickly stopped in the course of his cooling, and what does stop him is liquefaction!

Let us see diagrammatically what is the principle of these wonderful *exchangers of temperatures* of Siemens, which must be effectively counted among the most remarkable instruments of applied physics, and are to-day the foundation stone of all the apparatus which effect the liquefaction of permanent gases.

The compressed air is delivered through a pipe A (Fig. 1) to the expansion apparatus.

This, in the original idea of Siemens, was essentially a simple compressed-air motor, identical with a steam engine, and whose efficiency we have foretold above.

The air, therefore, is cooled in this machine by means of expansion and is then circulated in the tube B, concentric

to A, which it traverses in the *contrary direction* to the ingoing compressed air. During this inverse circulation the expanded air is heated naturally at the expense of the compressed air; it issues at the temperature of entry of the compressed air, having yielded up to the former theoretically all, and practically nearly all, its heat. The compressed air, therefore, reaches the machine a little cooler than the air that preceded it, and produces by its expansion a slightly lower temperature, cools the compressed air which

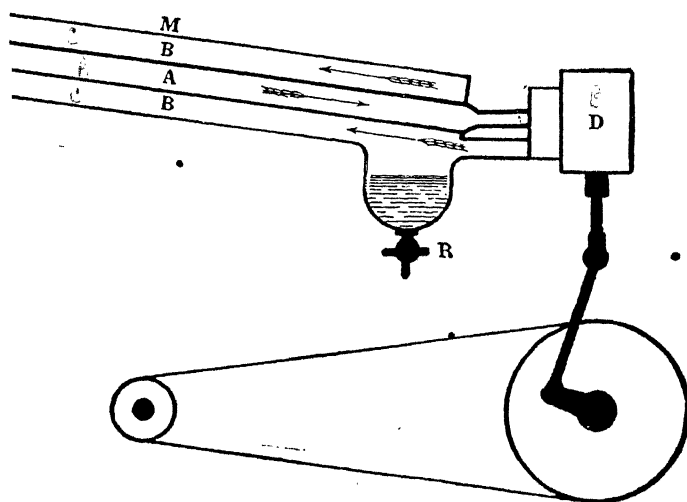


FIG. 26.—Scheme for the working of an exchanger of temperatures.

follows it a little more, and so on. Thus, by this admirable device, the temperature, of itself, is progressively lowered, and in such a way that at a given moment liquefaction is reached, and this terrible liquefaction of the permanent gases, which was foggy up till now, as we have repeatedly seen, and beset by innumerable difficulties, is reached.

**“Twixt cup and lip.”**—But a reflection will occur to the reader: Siemens’ process, as we have seen, is over half a century old. Why has it not passed its tests sooner? How is it that from its inception we have not been spared all the efforts which we have related?

the liquefaction of permanent gases, it would be necessary to compress these under enormous pressures, both very wasteful and very dangerous. Cailletet, in laboratory experiments, could venture to do this. In manufacturing it would not be permissible, all the more since only an infinitesimal portion of the gas expanded can be liquefied in this way.

On the contrary, if we limit ourselves to low pressures only, the lowering of temperature will be very limited, and will not lead very far along the road to the distant regions which have to be reached for liquefaction.

This dilemma seems embarrassing.

Happily, a precious device, thought of in 1857 by Siemens, allows us to amplify as much as we like the initial cooling furnished by the expansion. As much as we like, with the reservation that Siemen's conception, we must not forget takes us back to a period when—Faraday's ideas notwithstanding—the theory of permanent gases was completely unquestioned.

In reality, when following the letter of Siemen's programme, the operator is very quickly stopped in the course of his cooling, and what does stop him is liquefaction!

Let us see diagrammatically what is the principle of these wonderful *exchangers of temperatures* of Siemens, which must be effectively counted among the most remarkable instruments of applied physics, and are to-day the foundation stone of all the apparatus which effect the liquefaction of permanent gases.

The compressed air is delivered through a pipe A (Fig. 5) to the expansion apparatus.

This, in the original idea of Siemens, was essentially simple compressed-air motor, identical with a steam engine, and whose efficiency we have foretold above.

The air, therefore, is cooled in this machine by means of expansion and is then circulated in the tube B, concentric

to A, which it traverses in the *contrary direction* to the ingoing compressed air. During this inverse circulation the expanded air is heated naturally at the expense of the compressed air; it issues at the temperature of entry of the compressed air, having yielded up to the former theoretically all, and practically nearly all, its heat. The compressed air, therefore, reaches the machine a little cooler than the air that preceded it, and produces by its expansion a slightly lower temperature, cools the compressed air which

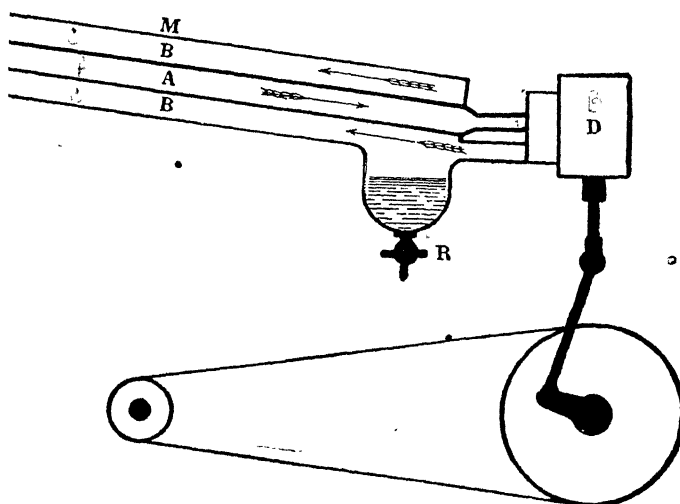


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**“Twixt cup and lip.”**—But a reflection will occur to the reader: Siemens’ process, as we have seen, is over half a century old. Why has it not passed its tests sooner? How is it that from its inception we have not been spared all the efforts which we have related?

It is because this process, like so many others, so perfect on paper, supported with much greater difficulty its trial in practice, that Siemens tackled it in vain, and a number of other experimenters—Solvay, Hampson, Thrupp, etc.—whom the apparent simplicity of the question had made enthusiastic, and who spared no efforts between 1857 and 1900 to solve it, have uniformly seen all their efforts fruitless.\*

It is in the course of the progressive cooling which would lead us to liquefaction that grave difficulties arise and nullify all the efforts of the experimenter.

It is the heat of the environment, which only requires to penetrate the interior of the machine to destroy all the cold produced; it is the heat evolved by the friction of the moving parts, which acts in a similar fashion; but it is *above all* through the progressive congelation of the materials used for lubricating, and the impurities taken in, when the gas is not perfectly purified and dried; and if congelation starts modestly by rendering more difficult the working of moving parts—such as cocks, valves, etc.—it culminates shortly in completely paralysing the working of the machine.

To give an idea of these difficulties, we must mention that one of the most conclusive of his experiments,† Solvay, a well-known inventor of the method of manufacturing soda by the ammonia process, which has revolutionised the chemical industry, reached with great difficulty —  $92^{\circ}$  C.!

Other experimenters were not even so well favoured, and it is not astonishing that with check following check they have ended by being convinced of the practical impossibility of expansion in machines of this type. In fact, Pro-

\* We ought to also recall the name of Armengaud, jun. (1872), who, although living, at this remote epoch, at the liquefaction of air, but at the simple production of cold, by whom the advantages of expansion with external work have clearly pointed out.

† R. 1893.



fessor Linde, making himself the mouthpiece of this state of mind, had no hesitation in expressing himself in the following terms :\*

“The realisation of the process (which is indisputable in theory) is disputable in practice for the following reasons : Suppose the process to be applied to atmospheric air down to the temperature which must be reached for liquefaction at that moment. We have present in the solid state all the substances mixed with the air, such as water, carbonic acid, etc., as well as all the lubricating materials employed. Under these conditions the working of a cylinder in expansion, with these distributing adjuncts, becomes almost impossible to secure. All those who have worked with these low temperatures know how many difficulties the working of a simple cock already presents. Furthermore, it would be very difficult, not to say impossible, to protect effectively at these low temperatures the expansion cylinder and its mechanism from the effect of external heat.”

Thus on this side the way seemed barred, and the year 1895 was reached without appreciable progress. Nevertheless, the failures themselves were not unfruitful; they are rarely otherwise in the hands of wide-awake observers. There is always some profit to be drawn from the most disconcerting experiment, and through the clear appreciation of the difficulties encountered, some solution far removed from the original idea is often evolved.

This was the case here.

**Joule and Thomson's experiments.** — The horizon which was the goal of the experimentalists had appeared to them, in these attempts, under such seductive colours, the possibility of attaining at liquid air, without any other means of action save compressed air itself, appeared to them so superior to all the processes till then known, that this question of expansion was examined from all points of

\* ‘Génie Civil,’ 1896.

view. In 1895 Professor Linde, shortly followed in England by Hampson,\* and in the United States by Tripler, found in an ancient and classical experiment in physics the foundation of an extraordinarily ingenious and elegant process. Probably we ought to attribute to the reduction itself of the new method, the secret of the over-easy giving up, by these various scientists, of the method of expansion in a motor engine.

The experiment in question is due to Joule and Thomson. It essentially consists (Fig. 27) in causing compressed gas to expand by making it flow out without sensible velocity across a porous diaphragm. If we had to deal with a perfect gas following exactly the laws of Mariotte and of Gay-Lussac, the theory—which we shall

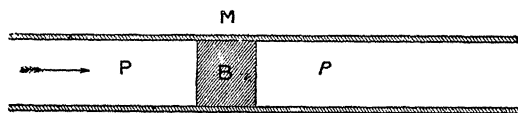


FIG. 27.—Joule and Thomson's experiment.

outline presently—would indicate that these gases *should not get cool* at all during such expansion. Only as real gases are not perfect, a slight cooling does take place—except in the case of hydrogen and helium—a cooling all the more sensible the less perfect is the gas, and which is very apparent with air itself, with which the cooling “*d*” for fall of pressure of  $(p_1 - p_2)$  atmospheres is given by formula determined by Joule and Thomson themselves:

$$d = 0.276 (p_1 - p_2) \left( \frac{272}{T} \right)^2,$$

which  $T$  is the *absolute* temperature of expansion, that

In point of fact the original patent of Hampson (English Patent 10,165, May 1, 1895) antedates by about fifteen days Linde's application (German patent 24, June 5th, 1895), but in his provisional specification Hampson only alludes to the usual circle of expansion of compressed air, that is, doubtless to its expansion in a machine. It was only in the final specification, deposited after the success of Linde's experiments, that the idea of expansion by simple outflow was introduced.

is the temperature counted from absolute zero by adding to the centigrade temperature  $273^{\circ}$ .

We thus see that the fall of temperature " $d$ " depends on the fall of pressure  $p_1 - p_2$  on the initial scale of  $\frac{1}{4}$  of a degree per atmosphere of fall; further, the lower the temperature, the larger the fall of temperature caused by expansion, since  $\tau$  becomes less. This is evidently the consequence of the fact that the colder the gas, the less perfect it becomes, but we shall see (p. 145) that we cannot utilise this fact as much as we might think with expansion carried out at the temperature of liquid air, and that really we can hardly benefit save from cooling corresponding with the ordinary temperature.

Now, this cooling at ordinary temperature is assuredly not enormous, certainly not to be compared with that which can be produced by adiabatic expansion in a machine with a piston, for example, which is theoretically given by the formula—

$$\frac{T_0}{T_1} = \left( \frac{p_1}{p_2} \right)^{0.29}$$

which, for a fall of from 40 to 1 atmospheres, yields only  $10^{\circ}$  C. with the first method of expansion, produces with the second a cooling of over  $175^{\circ}$  C. It is because of this enormous difference of efficiency, that as we have seen (p. 74), the expansion of air from 10 atmospheres through a valve produces no visible effect, while the expansion of this same air from 10 atmospheres in a motor produces a cooling effect of extreme energy. All this does not prevent, however, that subject to the condition of starting from high pressures, this process will bring about an appreciable fall of temperature; if this fall of temperature be supplemented with the use of an exchanger of temperature resembling the one whose principles we have described, it is perfectly capable of bringing about liquefaction.

By this means, we shall have realised an apparatus in which all the difficulties pointed out just above by Linde will have vanished, since thanks to the skilful use of a purely physical property of air, the expansion apparatus will have been reduced to a simple valve, that all moving parts will have disappeared, and, therefore, we shall no longer have anything to fear from the freezing of lubricants. Finally, we shall have devised a statal apparatus which is easy to insulate from the calorific point of view.

This is the truly seductive solution at which the experimenters we have named called a halt.

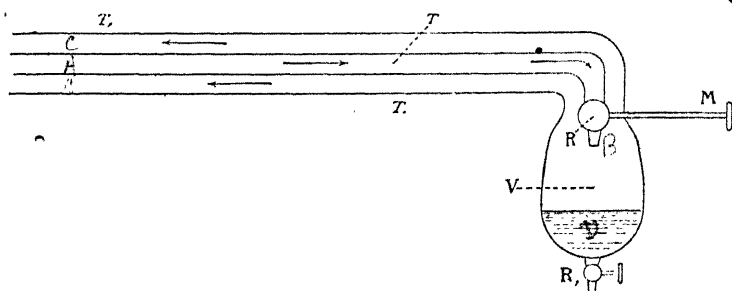


FIG. 28.—Diagram of Hampson's expansion.

The essential inconvenience of the process is, that it fails, because of its low efficiency, the compression of the air to enormous pressures, 200 atmospheres and over, and that it is on this account, notwithstanding Linde's admirable work, very uneconomical.

**Hampson's process and apparatus.**—Hampson's apparatus is without doubt the simplest of all liquid air appliances. Diagrammatically, the following is its description, from which we can appreciate its excessive simplicity.

It consists, first, of a two-stage compressor designed to bring the air to the high pressure indicated above. The compressed air, which is as a preliminary freed of its moisture and its carbonic acid by circulating slowly

through tubes filled with pieces of potash, is led to the expansion valve *v*, after having traversed a copper tube *T* (which in reality is of great length and a few millimetres in diameter), bent into a spiral and forming a singularly efficient exchanger of temperatures. The air

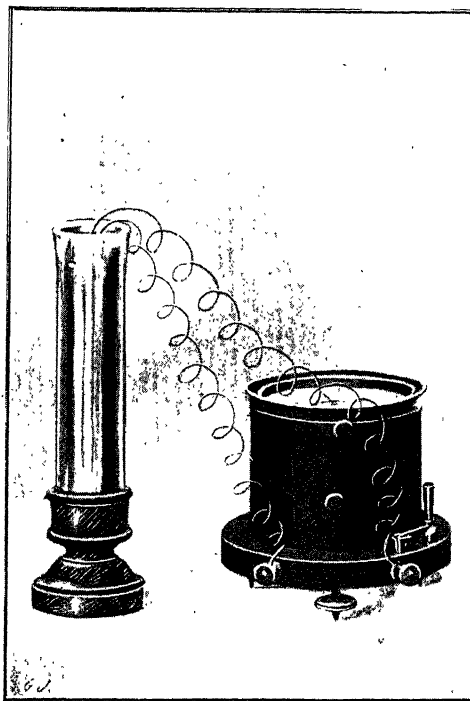


FIG. 28A.—Measurement of low temperatures by means of an electric thermometer.

expands in the chamber *v*, where its pressure falls down to atmospheric pressure; it is subjected thereby to a cooling which, according to the formula already given above (p. 81), we are able to calculate beforehand, in the neighbourhood of  $50^{\circ}$ , or at most one step in the gigantic stage we have to travel to reach liquefaction.

But the exchanger of temperatures now comes into play.

The expanded air is sent to circulate round the tube *T*, in the opposite direction to the compressed air, in a definite methodical way, by means of suitably disposed baffles.

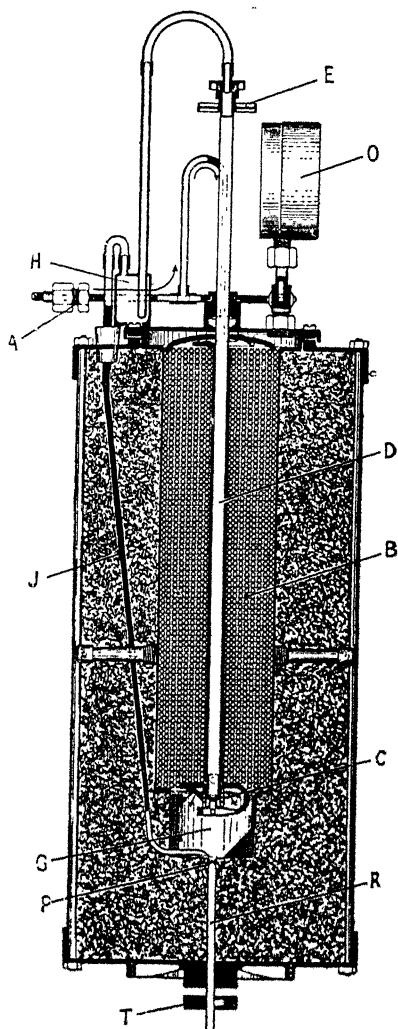


FIG. 29.—Sectional view of Hampson's laboratory apparatus.

Through the effect of the exchange of heat thus arranged the expansion temperature is lowered with extreme rapidity, shown by the increasingly rapid deviation of the galvano-

meter (Fig. 28A) connected with a thermo-electric couple soldered to the wall of the expansion chamber.

In about ten minutes, with the current type used in the laboratory,  $-193^{\circ}$  C. is reached, the temperature of liquid air under atmospheric pressure. From this moment onwards a portion of the expanded air is spontaneously liquefied and collects in the recipient *v*, where its level is indicated by a typical device, to which we shall have occasion to revert (p. 318).

A step, that is all.

And on this occasion it is no longer the question of a very efficient appliance, on paper, but of an apparatus which is absolutely practical, distributed by dozens of examples in laboratories (Fig. 29). It is impossible not to be astonished once more—we must be excused the repetition—at the immeasurable trouble that physicists have had to arrive at the liquefaction of the permanent gases. So true is it, that there is nothing more simple than a problem which is solved.

Be it remembered, however—and this is a general remark applicable to all appliances working at these extreme temperatures—all the cold parts of the apparatus must be very carefully protected against the penetration of the surrounding temperature by a thick covering of insulating material, which is generally hidden from sight by a metallic envelope, either painted or polished.

**The exchanger is not only an amplifier of refrigeration.**—It is important we should clearly understand the capital part played by the exchanger of temperature. We, up to the present, have only recognised in this appliance a device adapted to the extension of cooling and enabling thus the temperature of liquefaction to be attained. Now, the part it plays is far from being limited to this.

Without its use we should be condemned to the loss of almost the whole of the cold produced, even if, like Cailletet, only in a continuous way, we compressed the air to a suffi-

ient pressure, and submitted it to a sufficiently effective expansion to attain liquefaction directly. Whatever we did in point of fact, only a portion of the air would be liquefied, and even a very small portion thereof, all the rest leaving the apparatus at its actual temperature of  $-190^{\circ}\text{C}.$ ; here would result therefrom an enormous loss of cold. By, on the contrary, making this residual air pass through the exchanger, we succeed in communicating almost all its cold to the entering compressed air, which, while not requiring thereafter any save an infinitely smaller pressure, is thereby liquefied in a much greater quantity; the expanded air, on its side, escapes into the atmosphere at temperature only inferior to that of the entering air by some few degrees.

In well-constructed exchangers we are able to secure in manufacturing liquid air a difference of only  $3^{\circ}$  to  $4^{\circ}\text{C}.$  between the temperature of the entering air and that of the escaping air, that is to say, that during the short passage of a few seconds through the exchanger, the escaping air is heated from  $-190^{\circ}\text{C}.$  to very nearly the temperature of the surrounding air!

It is to this remarkable efficiency of Siemens' exchangers, we must repeat, that the manufacture of liquid air owes the greater part of its success.

It is well to observe in this connection that two favourable circumstances combine to bring about this very remarkable heating of the escaping air. On the one hand, we shall see that the calorific capacity and specific heat of compressed air *rapidly increases* when its temperature is lowered, while the specific heat of the expanded air preserves whatever may be its temperature the low normal value of 0.24. The result is, therefore, that when the air reaches the cold end of the exchanger, it has been much less cooled than the expanded air has been heated during the contrary passage. It is delivered, for example, at a



temperature of  $-140^{\circ}$  C., as against  $-190^{\circ}$  C. for the expanded air. There exists thus between the two streams of air a difference in temperature much greater than if this fact did not exist, very much greater even in the coldest stages, and this is manifestly a circumstance which favours the transmission of the heat of the compressed air to the expanded air.

Another circumstance which, in tendency, acts in the same direction, is that the expanded stream of air is also diminished, in proportion to the stream of compressed air, by all the portion subtracted in the form of liquid air; the mass of heating air being in excess compared with the mass of air to be heated, the heating of the latter may be perfect, and thus might escape from the apparatus without taking away, so to speak, one particle of cold produced at the other extremity of the expansion. This last circumstance does not exist, as we shall see, in the manufacture of oxygen by liquefaction, for here there is no longer any liquid air withdrawn from the apparatus, and the stream of the separated gases is exactly equal to the stream of the entering gases. It is in consequence of this fact that the exchangers of the Claude apparatus, which currently start with  $4^{\circ}$  C. of difference at the initial filling of the apparatus (working with liquid air), have this difference increased to  $5^{\circ}$  or  $6^{\circ}$  C. in the manufacture of oxygen.

**Linde's process and apparatus.**—The Hampson process is unquestionably admirably simple. It is, on the other hand, of low efficiency. The expenditure of 5 h.p. on the piston of the air compressor corresponds to a production of 1 litre of liquid air per hour, and this yield does not notably increase with the dimensions of the apparatus, so that the Hampson apparatus has not got away from the limits of the laboratory, while we must, however, recognise on the other hand the advantages conferred on it by its simplicity, its handiness, and the extreme rapidity with

which it is capable of furnishing liquid air—ten minutes, we have said, from starting.

In another process, far more elaborated, Dr. Carl Linde, professor of the Polytechnic School of Munich, an eminent specialist in questions of low temperatures, since the Linde ice machines form one of the most reputed types known in the field of refrigerating appliances—Dr. Linde, we should remark, starts also from a pressure of 200 atmospheres. But he expands his air no longer down to atmospheric pressure, as Hampson did, but down to 40 or 50 atmospheres only, and we shall see (p. 150) that this is indeed one of the most remarkable characteristics of this process.\*

Fig. 30 represents a model machine intended for laboratories, able to produce 1 litre about of liquid air per hour. In this figure *e* is a compressor, taking air from the atmosphere and compressing it to 40 atmospheres; *d* is another compressor worked by the same motor, and taking the air from *e*, as well as that returned from the apparatus, to bring their pressure from 40 to 200 atmospheres.

From *d* the compressed air passes into the bottle *f*, where it gets rid of nearly all its moisture, thence into the form *g*, which is plunged into a refrigerating medium, whose function we shall describe later (p. 150) in respect to its cold-producing efficiency, and where, furthermore, the balance of the moisture is retained in the form of rime, instead of being allowed to go and stop the tubes or valves of the apparatus.

In this connection we must observe that the perfect purification of the air, treated is one of the most essential

\* In the course of 1895, Professor Linde worked his first apparatus before the physicists and chemists of Munich, and a number of publications followed in the public journals during this same year. In 1895 Dewar produced a small apparatus based on the John-Thornton effect, and in the month of April, 1896, Hampson had his first small apparatus working at Brin's Oxygen Works, and at this same epoch introduced in the final specification of his patent the idea of expansion by simple outflow.

operations in the process of the liquefaction of air. We can well understand, in fact, what the least trace of impurity escaping with each kilogramme of air, slowly condensed and accumulated in narrow passages during operations which are often prolonged for *a week*, might succeed in doing at the end of such a lapse of time. It seems that this operation is treated somewhat offhand in the apparatus

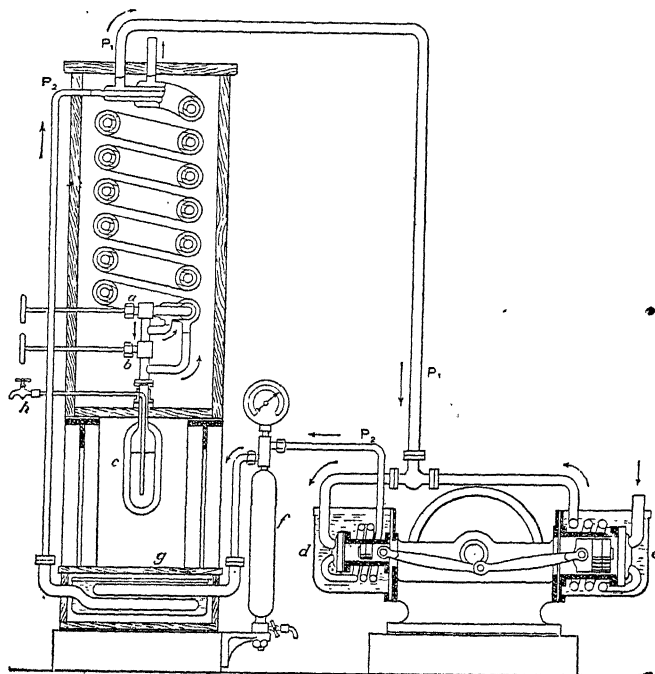


FIG. 30.—Linde machine, laboratory type.

which we have been studying, but we must recollect that the apparatus is destined for laboratories where experiments are not generally of long duration.

The dried and compressed air ascends then to the top of the apparatus and enters through the smaller of the three concentric worms, which compose in this case the exchanger of temperatures; it arrives in this way at the needle valve *a*, where it expands down to 40 atmospheres

while it gets cooled. This valve is the soul of the apparatus; in practice it is often necessary to manipulate it in accordance with the pressure-gauge readings to keep even with the obstructions, due chiefly to solid carbonic acid, which no special precautions had been introduced with the object of eliminating.

The air expanded to 40 atmospheres is returned to the compressor *d* through the second concentric worm; it parts with its cold in this way to the compressed air, so that the temperature in this case, also indicated by the electric thermometer, fastened to the exhaust, progressively goes down, and finally attains such a value that a portion of the air liquefies in the course of expansion and accumulates in the recipient. This liquid air is collected at atmospheric pressure in the recipient *c* by the discontinuous working of the valve *b*. But in falling from 40 atmospheres, the pressure at which it was produced, down to atmospheric pressure, this liquid air undergoes violent evaporation, which cools it from about  $-140^{\circ}$  C., the boiling temperature at 40 atmospheres, down to  $-190^{\circ}$  C. about, the temperature of evaporation at atmospheric pressure (p. 9). So as not to lose the cold of the evaporated gases these are led to the third concentric worm of the exchanger, and their cold is thus recuperated.

The whole apparatus is placed in a casing of wood filled with sheep's wool, which protects it from external heat. It calls upon the experimenter's patience more than Hampson's apparatus, and does not furnish liquid air save after an interval of about half an hour.

For reasons which we shall have to consider at length later, the yield of this remarkable apparatus, which we have been considering, is fairly high. In a big apparatus it reaches to a little over 0.5 litres of liquid air per half-hour, which represents well over the double of what is realised by the Hampson apparatus.

This result, in any case, applies to machines producing 50 litres per hour, of which many examples have been made, which shows moreover that with a Linde machine, and for the first time, we are in a position to leave the laboratory and invade the manufacturing field.

In 1899 a machine of this capacity was to be seen in Rhénania works at Stolberg, where it was in use for chemical manufacturing experiments, which were no doubt somewhat premature, and do not appear to have been followed up.

It should be also remarked that the considerable yield indicated above required for its realisation the employment of an auxiliary frigorific machine, which is one of the attractive features of Linde's method, and whose utility we shall explain further on (p 150). In the laboratory apparatus described above, the complication introduced by this auxiliary machine could be avoided by the employment of a worm immersed in a refrigerating mixture, but in the manufacturing machines this means becomes inapplicable, and has to be replaced by the use of an auxiliary ammonia machine, which really takes away from the Linde apparatus some of the simplicity of Hampson's machine, but which endows it with absolutely decisive advantages.

Fig. 31 shows the addition of such a frigorific machine to the Linde liquid-air machine in the laboratory of d'Arsonval, at the College of France. The ammoniacal vapours compressed in the compressor L, after having passed through the condenser worm, where they are liquefied in a water bath, and delivered, in the opposite direction to the dry compressed air, to a large tube concentric with that carrying the air and outside it, where they evaporate under the suction of the pump L.

The cold produced by the evaporation of the liquid ammonia energetically cools the compressed air, which reaches in this way the exchanger F at about  $-50^{\circ}\text{C}$ . On

On the other hand, the cold which evidently remains under these conditions in the expanded air, when it issues from the exchanger F is utilised for a preliminary cooling of the compressed air in the exchanger D. The utility of the supplementary cooling thus realised will be appreciated when it is known that from 5 litres per hour without an auxiliary frigorific machine the yield in liquid air of the installation rises to 8 litres with its aid.

We will explain further on what at first blush are the apparently mysterious reasons for such a result.

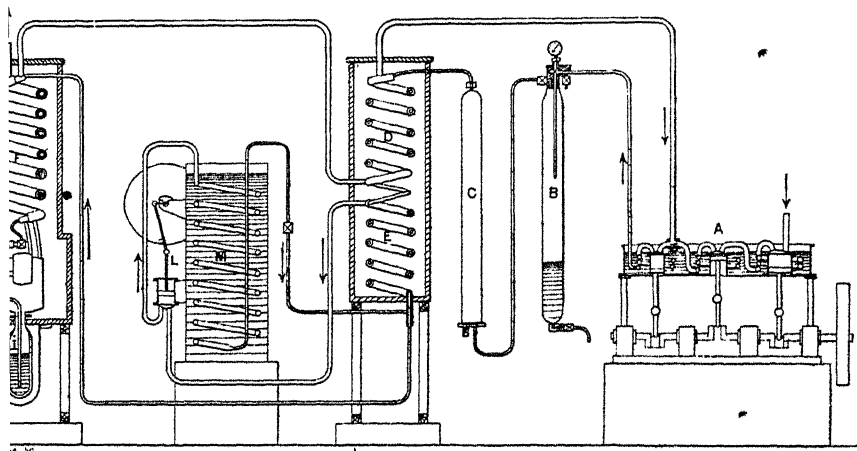


FIG. 31.—Diagram of the Linde installation at the Paris Exhibition of 1900—  
L M D F being the auxiliary refrigerator.

Fig. 32 is a general view of this installation as it appeared at the Paris Exhibition of 1900, where it was exhibited before being purchased by the College of France.

### IN PARENTHESIS.

Such was the condition of affairs in 1899, when Claude himself first took up the question.

How he came to direct his attention to this problem is a matter which it may not be without interest to describe briefly. Certain of our readers may perhaps know the work

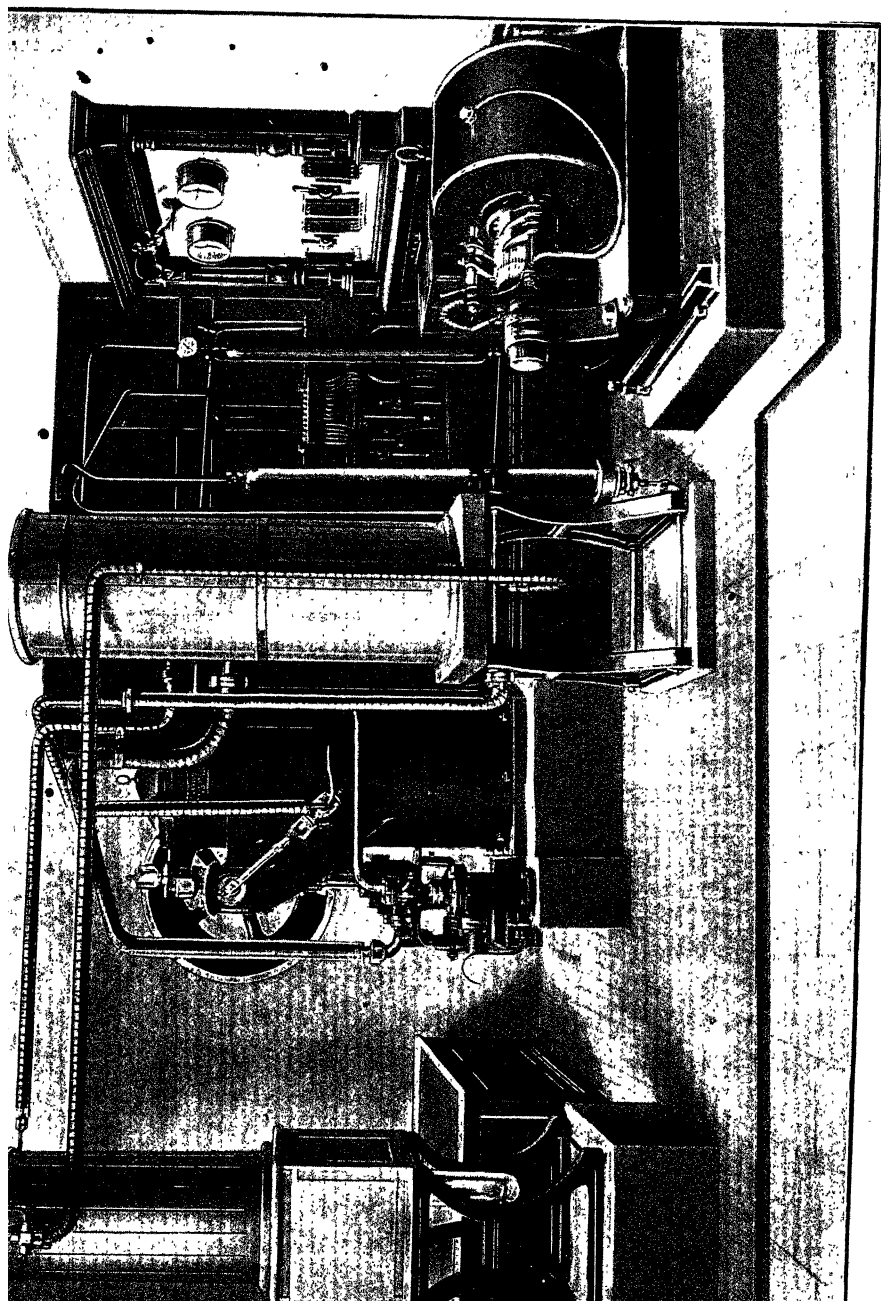


FIG. 32.—View of a 1900 Linde installation at the present time in d'Arsonval's laboratory at the College of France.

which he undertook from 1895 to 1896 in connection with acetylene, in collaboration with A. Hess, and which resulted in a method of storing this gas well known nowadays as *dissolved acetylene*.

This method of storing and transporting acetylene has shown itself very valuable in practice. It frees the consumer, in fact, from the endless trouble of making acetylene from carbide of calcium, while, at the same time, very different from the terrible liquid acetylene, it does away with all danger of explosion in the recipients. The solution of acetylene in acetone can stand without any difficulty, as has been demonstrated, which was confirmed by Berthelot and Vieille, the very crucial test consisting in electrically heating a platinum wire to a red heat in the centre of it.\*

Also, this process, adopted at the present time in France, Germany, Great Britain, and the United States, is being quickly developed for lighting motor cars and railway trains, for the autogenous acetylene soldering of metals, &c. During many years, however, its development has been suspended, as much through the ideas themselves which have accompanied the popularisation of the process, by the French company for dissolved acetylene, as by various adverse financial circumstances, among which was the high price of carbide of calcium.

Now it came into Claude's brain that electricity only played the part, in the manufacture of this remarkable product, of furnishing the temperature required for its formation, and that it might be possible to obtain this temperature by other means and in especial by the combustion of carbon in oxygen. As the latter exists in the air in the condition of a simple mixture, and therefore—as Claude thought at that time—no theoretical objection could assign any limit to the cheap price of its extraction, he

On many occasions bottles full of dissolved acetylene have been found intact after the débris of a fire.



foresaw the possibility of founding thereon a manufacturing process, purely thermal in character, and very economical in carbide of calcium.

This reasoning after all was fallacious only in two directions:

First, by falling into the fallacy—remarkably prevalent, we believe—that the separation into its elements of a gaseous mixture does not theoretically require any energy, Claude was committing an error. Really, and this will be demonstrated later (p. 290), such a separation calls for, even theoretically, a notable expenditure of energy. If he had known this it is very possible that he would not have so completely *tied himself up in a knot*. In certain ways misfortunes are a Godsend, and his ignorance, for once in a way, turned out very useful, since the theoretical necessity for expenditure of energy does not interfere with the *practical* yield of the extraction of oxygen from the air by the method of liquefaction from becoming wonderful through a combination of particularly favourable circumstances.

But if what precedes caused things to be seen of too rosy a colour, it was manifestly on the other hand, seeing them through the small end of the telescope when placing oneself at the very special standpoint of the manufacture of carbide of calcium. A more careful examination could not fail to show Claude that commercial oxygen, if necessary, could be called to play a part of very different importance. Clearly foreseen, ever since 1867, by Claude's estimable forerunner, Tessié du Motay, and by that other scientific man to whom we have already paid homage, Chas. Tellier,\* all this did not prevent 1898 being for Claude the starting point and origin of a conviction which he expressed in the 'Cosmos' of October 30th, 1897, in words which it may be interesting to recall some fifteen years later:

"Since," Claude wrote, "oxygen surrounds us on all

\* 'L'Ammoniaque,' by Chas. Tellier: J. Rothschild publisher, Paris, 1867.

## THE COMMERCIAL LIQUEFACTION OF AIR

des with such abundance, under the form of the simple mixture which constitutes the atmosphere, it is absolutely admissible that we should not arrive, sooner or later, at a physical process for its separation."

Manifestly it would have been thenceforward unlimitably agreeable for Claude to be able to preach, backed by success, and it was effectively to the practical exploitation of that incomparable mine, our atmosphere, that he dedicated himself ever since 1896.

He at first sought the solution of this problem in the centrifugal treatment of air at very high velocities.\* As a matter of fact he failed miserably. He was very much astonished at the time; he thought that the difference in density of oxygen and nitrogen was sufficiently great to bring about, at velocities of some 100 metres per second which he employed, at least partial separation. His astonishment was diminished when he learned to appreciate its correct value the theoretical work of the separation of oxygen from nitrogen (p. 292), work big enough to be beyond the capacity of the simple fan which formed the main total of his appliances; and it is impossible to avoid a certain amount of scepticism, even at the present time, when considering the courageous efforts which inventors like the Italian, Mazza, have dedicated in their turn to the same subject.

Claude thereupon essayed to reach his goal by utilising the unequal solubility of the two elements of the air in liquids under pressure and at low temperatures.† Oxygen in fact, always much more soluble than nitrogen, and the quantity of gas dissolved increases with the pressure and with the cooling. By employing liquids which are hard to freeze but are good solvents, such as alcohol and its congeners, we should be able to dissolve considerable

\* G. Claude.—French patent No. 262,168, December, 1896.

† G. Claude.—French patent No. 281,022, December, 1898.

quantities of super-oxygenated air which by the diminished pressure would be thereafter evolved from the liquid after the fashion of carbonic acid in seltzer water. At the same time, because of the cold, the vapour tension of the dissolvent would be neutralised and the losses of liquid might be very slight. This was surely a step on the right road, and it was in 1898 that the occasion was first presented to Claude to make an incursion into the low regions of the thermometric scale with the aid of expansion.

Nevertheless, here also Claude only succeeded in registering a long series of checks, when the French press, always looking for successes, commenced to occupy itself with results obtained four long years earlier by scientific men, in the matter of liquid air. In point of fact, it was well known a long time previously (Dewar) that liquid air, because of the difference in volatility of its constituents, presented an easy way of separating its oxygen and nitrogen; but, at the time when the obtaining of the smallest drop of liquid air still remained a veritable prodigy, within the capacity of only the most up-to-date and best equipped laboratories, the work of Linde, of Hampson, of Tripler, as we have seen, had already transformed the operation into a veritable process of manufacture of quite remarkable simplicity and truly commercial scope. Claude got, without further delay, the impression that in this direction lay the solution of the problem which perplexed him, and forthwith threw himself into the breach, with all the more enthusiasm that he was able to discern some veritable omissions in the work of his predecessors.

In this way, therefore, if after his predecessor Parkinson,\* whose sole application was on paper, the honour of having opened the way for the commercial application of liquid air and oxygen pertains incontestably to Professor Linde. It was neither by a sudden whim nor by a "general post"—

\* British patent 4,411 of 1892 (see p. 306).

as has been hinted—that Claude investigated the question, and we must see in his work on this subject a natural and logical sequel to that which he had followed without interruption ever since 1895.

Now in the plan which he had formulated for himself importance was attached first of all to obtaining liquid air as economically as possible, and it was to this object that he dedicated himself from the outset.

Certainly the Linde machines—it is well to insist on this point—had already marked a superb advance. But their perfection itself authorised the belief that initially all had been obtained from the principle upon which they depended.

Expansion in a machine still remained. But we have seen the abortive attempts to which this had led and Dr. Linde's verdict in the case.

Was this verdict without appeal? Were we obliged to finally bow before the uncontested authority of the one who had given it, though corroborated circumstantially by that of other seekers—Siemens, Solvay, Hampson, etc.?

It did not appear so to Claude.

There is a rule in matters of scientific research, whose invariable application the history of progress affirms in indisputable fashion, and which Claude has always borne in mind. When a thing is possible according to theory, and only practical difficulties oppose its realisation, it is infinitely probable that these difficulties are not insurmountable: it is infinitely probable, that at the price of more or less time and more or less pains a means can be found which will permit of the thing being realised, and theory confirmed. Therefore, before everything, what does theory say?

Keeping strictly at the outset to the main issue it says the following:

**Superficial comparison of the two methods of expansion.**—One remark, to start with.

It has been observed just now (p. 74), that if the compressed air is cooled during its expansion it is because it always performs during expansion a certain work, the quantity of cold produced being exactly equivalent to the mechanical work performed by the compressed air during its expansion.\*

Nevertheless we must be on our guard.

However clear in point of fact the idea may appear to be which we have just expressed, it lends itself to confusion,

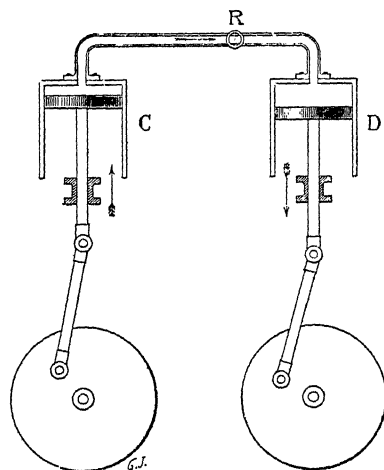


FIG. 33.—Direct transmission of energy from the compressor to the expander.

against which it is necessary to be forearmed. The work of expansion to be translatable into cold must be strictly that which the compressed air performs *by its own resources, by its own proper energy.*

We will explain :

Let us imagine that we carry out in the cylinder D of a machine (Fig. 33) analogous to a steam engine, the expansion of compressed air produced by a compressor; we introduce the compressed air at its full pressure  $p$ , during a portion of the stroke of the piston with a corresponding

\* This is only exact *approximately*; it is not altogether so, especially at high pressures, because air is not a perfect gas (p. 132).

volume  $v$ , then cutting off the admission, we allow the air to expand and thrust against the piston.

The work at full pressure is  $pv$ . Now this work has not been furnished, and cannot be furnished, by the compressed air from its own resources, since during the period of admission it remains always equivalent to itself and always compressed to the same pressure.

Whence, therefore, can this work take its origin? It takes its origin quite simply in the energy *directly transmitted* from the compressor through the gaseous piston rod of the pipe line, which, during all this period, behaves like

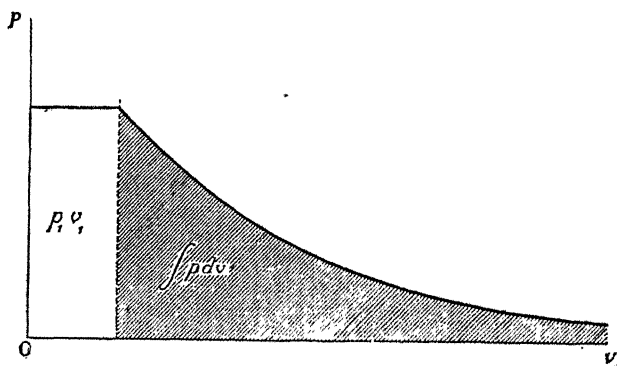


FIG. 34.—Analysis of the work in a cylinder.

a rigid rod and acts as a direct transmitter of the stroke of the piston of the compressor to the piston of the expander.\* It is manifestly evident that the work of thrust thus transmitted by the volume  $v$  under the pressure  $p$  is exactly equal to  $p_1 v_1$ .

This initiatory work  $p_1 v_1$ , wholly produced at the expense of energy other than that of the air itself which is expanded, cannot necessarily be translated into cold. The work of expansion, strictly speaking,  $\int p dv$  (Fig. 34), can alone count in the cooling, *i. e.* the work which the compressed air performs *by its own resources* irrespective of all external

\* This reasoning applies even when the compressor communicates with the expander through an intermediate reservoir.

agency, from the moment when the admission inlet is closed.

This reasoning is not at all modified if the expansion machine, instead of being placed immediately in series with the compressor, is divided therefrom by the exchanger, and if consequently the air reaches it very cold. The work of thrust is always  $p_1v_1$ , and is still furnished by the compressor. The case we have been examining is particularly simple, because the work furnished by the external energy (full pressure), is clearly separated from the proper work of the compressed air (expansion). It is not always thus—we shall presently see an important example of this—but it is manifest from this point onward that to obtain, in the case generally, a measure of the cold produced, we must deduct the effect of all external energy from the total work, performed generally during expansion, by the external energy and by the energy proper to the air (and in the total work of the air is included what we shall further on call the *internal work*); the calorific equivalent of the excess thus calculated is manifestly the measure of the cold.

This admitted, let us now seek in various interesting cases an expression for the work furnished by expansion. Let us consider, firstly, an isolated mass of compressed air expanding by its own means, as in Cailletet's apparatus (p. 53). Here, without hesitation, there is no external energy in play, all the work done is furnished by the expanding gas, therefore it must altogether be translated into cooling.

To enable expansion to take place, it is manifestly sufficient that the counter pressure which is opposed to the compressor gas is *inferior* to its own proper pressure. This counter pressure may therefore be great or small as we choose; it is very evident that the work which the gas has to effectively produce to realise a definite increase in volume will depend on the resistance of the counter pres-

sure which is opposed thereto during this increase. If this counter pressure be feeble, the work produced will be slight. If the gas is expanded *in vacuo*, the effect will be reduced to a momentary frigorific manifestation; the gas will then expand quickly and absorb in this way a considerable heat in the form of kinetic energy, but this energy will disappear very soon by giving up the calorific energy it has absorbed; and, on the contrary, the work furnished by the air will be as great as possible, if we can arrange so as to oppose thereto at each instant during expansion, an exactly equivalent counter pressure or one only slightly inferior to its residual pressure. This last case, moreover, constitutes in principle a reversible operation, while expansion against a pressure *inferior* to the initial pressure of the gas (Linde, Hampson, etc.) is essentially non-reversible,\* and acquires from this fact—we shall soon see this confirmed (Chap. VI)—a certain element of inferiority.

Thus, in a general way, the work of expansion is expressed, *independently of the pressure, proper* to the compressed gas, by  $W = \int p dv$ , in which  $p$  represents at each instant the *counter* pressure opposed to the gas in the increase of volume  $dv$ ; and so that this work shall be a maximum, we shall have to arrange, that during the whole course of the expansion the pressure  $p$  is a maximum, and that at each instant it is also as little inferior as possible to the residual pressure, proper to the gas under expansion.

Now, instead of the discontinuous expansion of a mass of isolated gas, which was able to furnish Cailletet with the admirable scientific result we wot of, but which was of no commercial interest whatever, let us consider the continuous expansion of compressed air produced by a compressor; the external energy furnished by the latter under the form of the continuous thrust of the column of air

\* Although it comprises a portion which is reversible in principle, viz., the external work.



which penetrates into the expansion apparatus must in this case be counted in.

**Expansion with external work.**—Let us first consider expansion in a cylinder of a machine analogous to a steam-engine. Let the work effected at each stroke of the piston be represented in the accustomed way by the diagram given below, the space moved over by the piston being the abscissæ and the pressures the ordinates (Fig. 35).

Here, as we have seen (p. 99), the work in the course of one stroke of the piston is divisible in two portions : the

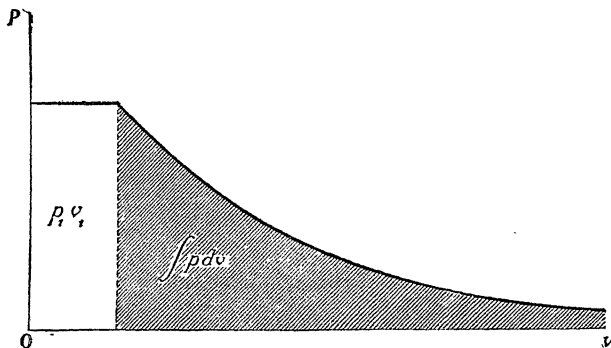


FIG. 35.

work at full pressure,  $p_1 v_1$ , and the work of expansion,  $\int p dv$ . So far as the first is concerned, as was observed above, during admission of the compressed air, this remains always identical with itself, always compressed to the same pressure; it cannot, therefore, produce from its own resources the work,  $p_1 v_1$ , expended during this period; and we have seen that this work is effectively entirely furnished by the compressor, and transmitted by the piston-rod formed in the pipe connections.\*

Therefore, the work at full pressure,  $p_1 v_1$ , *absorbs the whole of the external energy* directly transmitted by the

\* We know that habitually, in thermodynamic formulæ, the volume considered is that expressed in cubic metres of a kilogramme of water under the pressure and at the temperature in question. If  $v$  be expressed in cubic metres,  $p$  in kilogrammes per square metre,  $p v$ , will be expressed in kilogramme meters.

compressor to the outlet of expansion, and *does not count* from the point of view of the cold. *Per contra*—and for this very reason—the work of expansion,  $\int p dv$ , remains wholly available for cooling,\* and this work is very great, since it comprises the whole of the etched portion of the curve. It should be remarked, moreover, that as the expansion is effected against the piston of a machine working under load and furnished with a flywheel, a counter pressure exactly equal and opposite to the residual pressure exists, which is, as we have seen (p. 101), the necessary condition for the work of expansion being a maximum.

**Expansion by simple outflow.**—Let us consider, on the contrary, the expansion of a *perfect* gas by simple outflow without sensible velocity, from  $p_1$  to  $p_0$ . The only occasion for work involved here is the thrust  $\int p dv$  which the expanding gas must effect against the pressure  $p_0$  in the enclosure where the expansion is effected.

But this pressure  $p_0$  is in this case a constant, so that

$$\int p_0 dv = p_0 \int dv = p_0 v_0.$$

Thus the work of thrust for each volume of air corresponding to the volume of expansion  $v_0$  is  $p_0 v_0$ .

Now, a very simple reasoning will show us that this work is not translated into any cooling. Here is a very curious result, but we are enabled in this case to understand the reason. In this case also the compressor transmits work directly up to the orifice of expansion through the rigid piston formed in the connecting pipes, the work of thrust for an outflow  $v$ , at a pressure  $p$ , being always  $p_1 v_1$ ; and in this case also the energy must be entirely absorbed before there can be any question of cooling.

If we can show that the work of thrust which we have just estimated at  $p_0 v_0$  exactly equals  $p_1 v_1$  we shall at the

\* Except, be it understood, the portion of this work of expansion abstracted by friction, which simply disappears from the frigorific balance sheet, the heat evolved by this friction compensating exactly the cold produced by the work it has involved.

same time demonstrate that the expansion of a perfect gas by simple outflow from  $p_1$  to  $p_0$  does not produce any cooling. A direct demonstration being a little difficult, we shall have recourse to the following elementary reasoning, which will be quite sufficient for the case.

Let us *suppose* first that there is no effective variation of temperature during expansion; then as *ex hypothesis* we are dealing with a perfect gas, Mariotte's law is applicable, it follows therefrom that  $p_1 v_1 = p_0 v_0$ ; therefore the work effected  $p_0 v_0$  absorbs exactly all the external energy  $p_1 v_1$ ; therefore practically there is no variation of temperature, and this initial hypothesis does lead us to an absurdity.

Let us make, on the contrary, the *hypothesis* that there is cooling in the course of expansion. Then we unavoidably have  $p_0 v_0$  of less value than in the preceding case ( $p_0$  the same and  $v_0$  diminished) and consequently  $p_0 v_0 < p_1 v_1$ . The work of thrust is therefore *inferior* to the energy transmitted by the compressor and cannot therefore absorb it entirely; there would then be in this case heating, which is against our hypothesis—which is therefore absurd.

Let us finally suppose that there is heating; then  $p_0 v_0 > p_1 v_1$  the work of thrust is consequently *superior* to the energy transmitted; therefore cooling takes place; this is again a consequence contrary to the hypothesis, and here again we get to an absurdity.

The first hypothesis alone is therefore justified, and consequently, conformably with what we laid down, the expansion by simple outflow of a perfect gas is not translated into any cooling; it is vain therefore to expect to increase the work of expansion by increasing the pressure of thrust, as Pictet somewhat ingenuously suggests,\* because if  $p_0$  is thus increased,  $v_0$  will diminish proportionately, so

\* Pictet, 'The Theory of an Apparatus for Producing Liquid Air by Expansion,' Weimar, 1903.

that  $p_0v_0$  will always remain constant and always equal to  $p_1v_1$ .

And if Linde, as we have stated, nevertheless increases largely his thrust pressure by comparison with Hampson, it is for an entirely different reason, which we will appreciate later.

It will be understood that we insist on these points because they are errors of the Pictet kind which have continually led very competent engineers to cast doubt upon the advantages of expansion with external work—advantages which are going now to make themselves self-evident.

In effect we have just seen that the work of thrust of a perfect gas in expansion by simple outflow is equal to  $p_1v_1$ , *just as its work under full pressure in the cylinder described just now*. As in that case, its sole effect is to absorb the energy directly transmitted by the compressor, and similarly is not translated into any cooling.

Only there is a shade of difference.

In expansion against a piston the work under full pressure constitutes only *a portion* of the total work; doubtless it is not in itself a source of cold,\* but thanks hereto the work of expansion at least remains entirely available for cooling.

In simple outflow, on the contrary, the work of thrust is the only work we can dispose of, and it absorbs entirely the whole of the external work. We can see that the drawback is serious. It is irreparable for perfect gases.

\* And strictly speaking this is only a mode of expression justified by convenience of calculation, and it would be deplorable if it led to neglecting in any way the work under full pressure. In reality, there is not two kinds of work: each kilogramme metre abstracted mechanically equals  $\frac{1}{44}$  of a therm which disappears in the gas; if consequent upon faulty arrangements, excessive dead space, wire drawing of the gas, etc., the work under full pressure is not continuous, the output of cold would commensurately diminish; the correct way to estimate the cold, as we have said (p. 101) consists in taking all the work produced as a whole, external work included, then subtracting the transmitted external energy and calculating the calorific equivalent of the remainder, which represents the cold produced.

But perfect gases are happily only a theoretical fiction. Air is an imperfect gas; it does not entirely follow the laws of Mariotte and Gay-Lussac; it is due to this circumstance in appearance so insignificant, that Hampson and Linde owed their success.

We now see what an ample foundation expansion with external work offers, and how wise Claude was in determining to take advantage of it.

At the present time, nevertheless, the Linde process is very extensively adopted.

It is, with Claude's, the only process which has participated in manufacturing operations up to the present time.

We must, moreover, recognise the ability with which Professor Linde has been able to perfect the somewhat cranky basis which he chose for his starting-point. We have already narrated his successes; we must, to appreciate them with reason, describe exactly how they have been obtained.

The author craves the reader's indulgence for having insisted upon explaining in these pages the theory of liquid-air machines, still little known at the present time, in accordance with his personal ideas. This could not be done without a few integrals, in themselves very inoffensive. The reader who may wish to avoid considering them and to keep strictly to generalities, will only have to take the trouble to resolutely skip the two or three following chapters.

## CHAPTER V

### THE IMPERFECTIONS OF THE GASEOUS STATE AND THE WORK OF VAN DER WAALS

THE imperfection of real gases, as we have seen, constitutes the exclusive foundation of the technics of expansion by simple outflow. The fact itself that liquefaction is the objective aimed at, likewise indicates that this imperfection must also intervene in expansion with external work, and we shall shortly see that Claude had many a crow's pick with this fact in the course of his investigations.

It is therefore essential, before proceeding further, to define the sense of the vague expression "imperfection of the gaseous state."

It is manifest, *ab initio*, that Mariotte's law cannot remain indefinitely true when the compression of a real gas is pushed isothermically beyond any limit. We can very well imagine, moreover, that at first starting a gas, which is extremely dilated and diffused matter, should submit with docility to the effect of pressure, that it should become greatly contracted, and that in this way and for each slight pressures Mariotte's law should apply exactly. But as the pressure rises, as the gaseous molecules close in, finding them less at their ease in a smaller space, the compression must tend, it would seem, to become more insupportable\*; the gas will progressively be less com-

\* This simplified conception must be physically translated in the following fashion. I admit now that gases are made up of very small and very elastic particles constantly moving in every direction, rebounding one against the other or against the walls of the container with very great velocities varying from 1842 metres per second for hydrogen to 398 metres per second for carbonic acid. The pressure exercised by these gases on the walls of the container holding them is only the resultant of these impacts.

pressed than Mariotte's law lays down. And when, through a sufficiently energetic compression, the accumulation of gaseous matter becomes comparable with that of liquids or solids, which are so difficult to compress, it is most probable that the gas itself will no longer remain so to any extent.

Thus, at very high pressures, the volume must necessarily tend towards a limiting value, towards the *co-volume* corresponding to the volume proper of the molecules, and below which it is incompressible.\*

This conception of an irreducible volume or co-volume has been introduced in science by Dupré.

It is interesting to remark that this notion of infinitely condensed matter does not necessarily correspond to the idea we may have of a plenum or of close packing carried to an extreme limit. The marvellous discoveries of which the achievements of M. and Mme. Curie and of J. J. Thomson have been the tokens have, moreover, brought us strange suggestions on the constitution of matter.

The atom, the intangible but inert atom of our past beliefs, from henceforward appears to us as a solar system

NOTE.—If we were to reduce to  $1/n$  the volume of these recipients, the velocity of the particles, which is merely a function of their temperature remaining constant, the number of impacts per unit of surface becomes  $n$  times greater, for the calculus of probabilities shows that the *mean* path of a particle between two successive impacts against one wall or against another particle is in this case reduced to  $1/n$ , and that, therefore,  $n$  times as many impacts occur; the pressure therefore increases in proportion to the reduction of volume, which is Mariotte's law. But this is manifestly only true on condition that the dimensions of the molecules can be considered as *nil* by comparison with the mean path. Now by reason of the very large number of gaseous molecules (it is calculated that in a cubic centimetre there are about 20 millions of milliards) it is no longer so: this mean path between two impacts is extremely short, that is of the order of the ten thousandth of a millimetre, and the diameter of the molecules is not a negligible quantity compared therewith, especially in proportion as the gaseous volume diminishes. It results from this that the number of impacts increases *quicker* than the volume diminishes, which tends to make Mariotte's law incorrect in the same direction.

\* See Van der Waals theory: the co-volume is equal to four times the volume of the molecules.

n miniature; if we supposed it enlarged to the size of a cathedral, it would be composed of the vertiginous revolutions of some thousands of asteroids of the size of a pea, of some tens of thousands even, according to J. J. Thomson's most recent researches.

The unmeasured forces brought into play by the very rapidity of these rotations would render the constitution of the atom intangible,\* and although the atom itself still remains essentially rarified, in respect to this conception, our densest metals may be much less than a fugitive vapour; still this breath, this nothing, remains perfectly incompressible under the most enormous forces which human wit can yet bring into play. All that we can achieve through the application of these forces, acts on the inter-molecular spaces, and our power is limited to reducing these to nothing. It is in this connection that we could consider the notion of co-volume.

Thus according to our elementary conception, if an error in Mariotte's law is to be foreseen it lies in the direction of a *lesser* compressibility than that which the law presupposes should be found.

Well, let us submit the matter to the test of experiment, and exactly the contrary is what we find! The test was applied long ago (p. 24) to gases which are easily liquefied;

Excepting that of the instable atoms of radio-active bodies, which are undergoing slow but continual disintegration, and have permitted physicists to measure the life of this interatomic energy, whose order of magnitude has revealed itself to be millions of times greater than that of the most energetic of our chemical reactions. What a powerful means of action lies in this enormous source of energy which is at our disposal," wrote Claude in his 'Chats about Radium' in 1905: "what a priceless goal for our science, to demolish with these remains of atoms, these atomic projectiles, the so-called simple atoms of the elements of modern chemistry, to make the transmutation of substances re-enter the domain of natural laws!" Two years later Sir William Ramsay demonstrated these suggestions to be well founded, proving by quite exceptional experiments that according to the conditions under which we work, the emanations of radium can be transformed not only into helium, as he had already demonstrated in 1903 in his memorable transmutation, but also into neon or argon, while, transforming copper itself into iron and perhaps into sodium!



the permanent gases themselves, in which Dubong and Arago described faithful subjects of Mariotte's law, have been found by Regnault to be more compressible than the law required.

Hydrogen alone is the exception, but without Mariotte's law being able to score, because it is *less* compressible than the law requires. For all the other permanent gases, it is only in the case of experiments pushed on to high pressures, like those of Natterer (p. 41), that the *diminution* in compressibility clearly appeared.

The reason for this excess of compressibility is very interesting. It was guessed by Hirn.

We should see therein simply a manifestation of the law of universal attraction, Newton's celebrated law, which rules over the internal attractions of a modest grain of sand just as much as over the evolutions of the worlds in the universe.

Moreover, because of the relatively considerable distance apart of the gas molecules, the molecular attractions, inversely proportional to the squares of the distances, are very feeble at pressures which are not high.

But let the volume be diminished under the influence of external pressure and the molecular attractions will increase little by little, become appreciable, and finally energetic. They will therefore act as an *internal pressure*, which will tend to amplify, through mere approximation in the same way as the attraction of the armature for an electric magnet, and will come, consequently, more and more energetically to the support of the external pressure in diminishing the volume. Also this effect will exceed the opposite effect due to the close packing of the molecules and the gas will be compressed more than the law requires.

Numerous efforts have been made to take into account these two orders of facts in the characteristic equation for real gases, and to replace the Chapeyron relation by one more justified by facts.

$$pv = RT$$

is the simple derivative of the laws of Mariotte and Gay-Lussac and only applicable, therefore, to the theoretical case of perfect gases. In this equation  $R$  is, as we know, equal to  $p_0 v_0 / T$ .

The happiest attempt, the one that has been the most fertile in all sorts of consequences which the genius of its author has deduced therefrom, is that of Van der Waals.

According to the Dutch scientist the characteristic equation for *all* real gases is of the form—

$$\left( p + \frac{a}{v^2} \right) (v - b) = RT,$$

and  $b$  being particular co-efficients proper to each gas and  $R$  having the same value as in the preceding equation.

We can see, moreover, that this form of equation strictly embodies our explanations given above; the effect of the pressure  $p$  is completed in the first parenthesis by that of the term  $\frac{a}{v^2}$  which rapidly increases as the volume diminishes.

This term  $\frac{a}{v^2}$  is the *internal* pressure of the gas. It is easy

to understand that this corrective term well expresses the tendency of the gas to be compressed too rapidly when the pressure increases and the temperature  $T$  is constant;

because when this pressure is  $p$ , it is by  $\left( p + \frac{a}{v^2} \right)$  that  $(v - b)$  is to be multiplied to obtain the constant  $RT$ , which implies that this factor  $(v - b)$ , and therefore  $v$ , is less than it would be if  $p$  and  $T$  were acting alone.

The action in relation to the close packing of the molecules, to the progressive difficulty of compression, on the other hand, is indicated by the correcting term  $b$  of the second factor  $(v - b)$ , which is nothing else than the co-volume. So that the first member of the equation should, however, continue equal to  $RT$  when  $p$  increases indefinitely and  $T$  is constant, it is necessary that the second factor

$(v-b)$  should tend towards zero; therefore in the limit  $v-b=0$  or  $v=b$ : thus  $v$  tends towards the co-volume and not towards zero. This correcting term therefore expresses well, the tendency of the gas to be less compressible, and its influence is less than that of the previous factor for average pressures, except in the case of hydrogen, and becomes preponderating at high pressures, in agreement with the indications of experience.

Having in this way registered the two opposite tendencies which we have been analysing, we find that Van der Waals' formula, with, for each gas, a special value for the co-efficients  $a$  and  $b$ , realises the prodigious quality of being able to represent the condition of this real gas within the most extended limits, not only of pressure, but also of temperature, and to even comprise the upside down physical conditions which accompany liquefaction.\* Knowing, for example, the constants  $a$  and  $b$  of the gas under consideration in relation to Mariotte's law, constants obtained by experiments carried out at ordinary temperatures, it is possible to calculate by means of the formula the critical data of this gas, the temperature, volume and critical pressures, and the values thus calculated differ very little from the real values found by direct experiment. For certain permanent gases the critical values have thus been found, so to speak, before the event. This recalls rather the method of Le Verrier pointing out in the sky the still unknown place of Neptune, and, although less theatrical, the "gesture" of Van der Waals has not been less informing for science.

To understand how this predetermination is possible, let us first remark that by giving  $T$  in Van der Waals' equation a series of successive values and calculating for

\* Provided the theoretical fiction of Thomson's curles be admitted, which have not been, on the other hand, imagined expressly to meet the case, since Van der Waals' formula is three years older.

each of these values the curve of  $p$  as a function of  $v$ , we should obtain a series of isothermes (Fig. 36) which adopt exactly the general form of those obtained, for example,

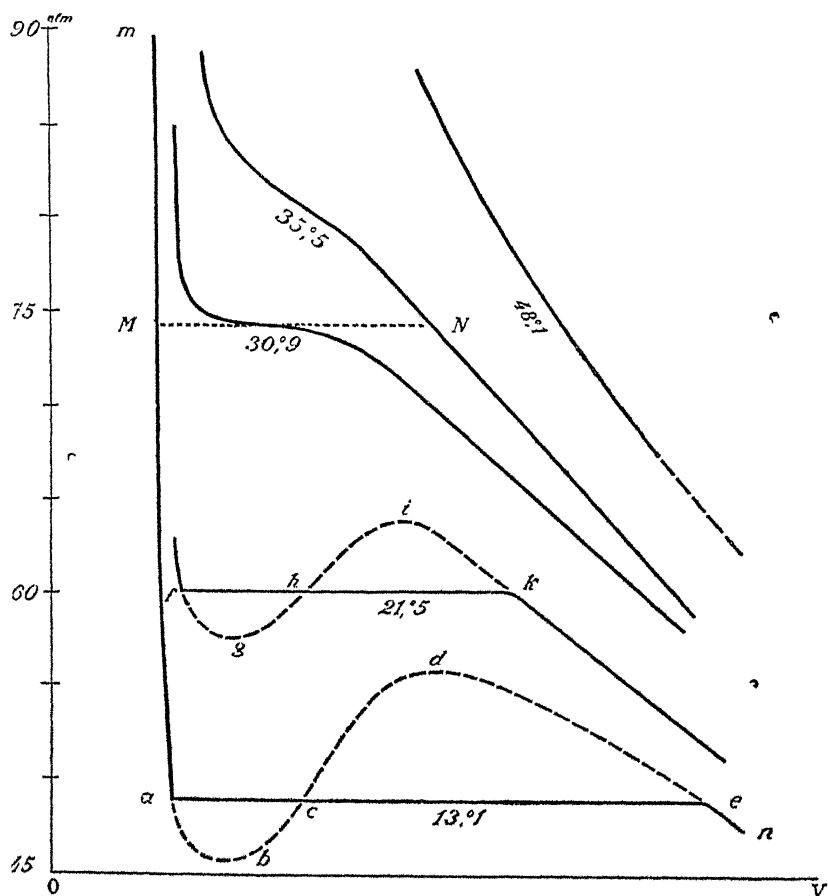


FIG. 36.—Andrews' curves with Thomson's curves.  $MN$ , tangent at the critical point.

by Andrews in his book on carbonic acid (fig. 20, p. 47). This trace at the unknown critical point will have a horizontal tangent  $MN$  cutting the curve (Fig. 36). This would be sufficient to determine this critical point graphically, but we shall see presently of what overpowering interest the analytical solution of the problem becomes.

Now, as we have already observed (p. 49), a tangent of this kind is characterised by the equation—

$$\frac{dp}{dv} = 0,$$

which indicates that the tangent is horizontal, and by this other—

$$\frac{d^2p}{dv^2} = 0,$$

which indicates that the tangent *cuts* the curve.

The position of this critical point will therefore be defined analytically by solving a group of three equations—

$$\left(p + \frac{a}{v^2}\right) (v - b) = RT, \text{ or } p = \frac{RT}{v - b} - \frac{a}{v^2} \quad (1)$$

$$\frac{dp}{dv} = -\frac{RT}{(v - b)^2} + \frac{2av}{v^4} = -\frac{RT}{(v - b)^2} + \frac{2a}{v^3} = 0 \quad (2)$$

$$\frac{d^2p}{dv^2} = \frac{2RT(v - b)}{(v - b)^4} - \frac{6av^2}{v^6} = \frac{2RT}{(v - b)^3} - \frac{6a}{v^4} = 0 \quad (3)$$

From (2) and (3) we get—

$$\frac{RT}{(v - b)^3} = \frac{2a}{v^3}, \text{ and } \frac{RT}{(v - b)^3} = \frac{3a}{v^4},$$

and by dividing each member by the corresponding member—

$$(v - b) = \frac{2v}{3}, \text{ or } v = 3b;$$

replacing in (2)—

$$\frac{RT}{4b^3} - \frac{2a}{27b^3} = 0, \text{ or } T = \frac{2a}{27b^3} \times \frac{4b^3}{R} = \frac{8a}{27bR};$$

finally substituting in (1)—

$$p = \frac{8aR}{27bR \times 2b} - \frac{a}{9b^2} = \frac{8a}{54b^2} - \frac{a}{9b^2} = \frac{a}{27b^2}$$

The values thus obtained are the critical elements of the gas in question, expressed in this way for the first time by Van der Waals as functions of the constants  $a$  and  $b$

only, of the gas with reference to Mariotte's law. Representing them respectively by  $V_c$ ,  $T_c$ , and  $P_c$ , we have—

$$V_c = 3b,$$

$$T_c = \frac{8a}{27bR},$$

$$P_c = \frac{a}{27b^2}.$$

We shall see, further on, of what absorbing interest these formulæ are (p. 122), and we should notice the particularly simple expression for the critical volume  $V_c$ , which is equal to three times the co-volume.

The verifications made by Van der Waals of his formula have been very numerous. Applying it, for instance, to carbonic acid, he thus found as critical temperature  $32.5^\circ$ , which does not differ widely from the value found by Andrews— $30.9^\circ$ .

We should state, however, that these verifications, at the already far-off epoch to which they apply (1873), could only be effected with the very limited means which science then possessed. When the work of modern experimentalists has enabled the list to be extended, it has been necessary, so as to bring the results closer together, to somewhat modify the form of Van der Waals' equation. Clausius in particular pointed out that the molecular attraction must diminish when the temperature is lowered. This scientist and Sarrau have put forward with this object formulæ which are applicable in a very satisfactory fashion, and by means of which, moreover, it has been possible to formulate all the laws which have shed so much glory on the name of Van der Waals. Sarrau, by utilising his formula for the representation of the results obtained for nitrogen, at ordinary temperatures, by Amagat, an observer who caused the memory of Regnault to live again, has even realised an interpolation without parallel in the history of science. He put forward as the critical data for nitrogen—

$T_c = -142^\circ \text{C.}$ ,  $P_c = 32.9$  atmospheres, while direct experiment was to furnish Olszewski, fifteen years later, with  $-146^\circ \text{C.}$  and 35 atmospheres, and Wroblewski with  $-146^\circ \text{C.}$  and 33 atmospheres!

It is therefore quite another thing than the vague, empirical formulæ that we find in Van der Waals' equation and its derivatives; it really constitutes a secret which Nature herself has allowed to escape her.

### CORRESPONDING STATES.

To the degree of approximation of which it admits, Van der Waals' equation is sufficient to allow us profitably to examine the behaviour of any gas in respect to compressability at different temperatures. The preferable method of investigation consists in constructing for each value of  $\tau$  the curve of  $v$  and  $pv$  values as functions of  $p$ , this curve constituting in this way the *isotherm* corresponding to the chosen value of  $\tau$ .

We obtain the following results:

(1) At a high temperature gases starting from feeble pressures are *less* compressible than Mariotte's law requires (Fig. 37). The  $pv$  curve, sensibly rectilinear, slopes upward forthwith. The effect of the co-volume preponderates in this case from the first over that of the internal pressure. This case is, moreover, closely that of hydrogen and probably of helium starting from the ordinary temperature of the air, because of the extreme smallness of their internal pressure.

(2) At a lower temperature, which is of the order of the temperature of the environment for permanent gases, excepting hydrogen and, no doubt, helium, the product  $pv$ , when the pressure rises, indicates almost at once an appreciable diminution (see the isotherm A, Fig. 38). The researches of Amagat and of Witkowski disclose this dimi-

nition in the case of air from atmospheric pressure onward (see table, p. 127), which shows that throughout this portion of the isotherm the effect of the internal pressure  $\frac{a}{v^2}$  preponderates over that of the co-volume  $b$ . This decrease in  $pv$  gets less little by little, and for a certain pressure, attained (Fig. 38) at M (isotherm A),  $pv$  passes through a minimum. By placing Van der Waals' equation in the form—

$$pv = RT - \frac{a}{v} + \frac{ab}{v^2} + pb.$$

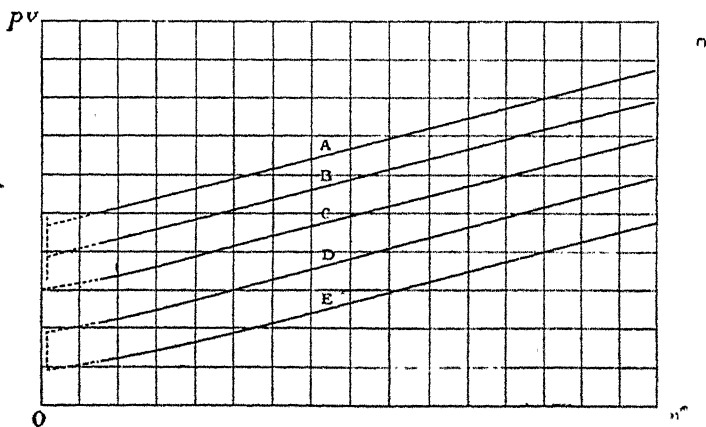


FIG. 37.—Compressibility of gases at high temperatures and of hydrogen at ordinary temperatures.

It can easily be shown that this minimum is attained when—

$$\frac{a}{v} = \left( \frac{a}{v^2} + p \right) b.$$

From this point onwards, the influence of the co-volume becomes preponderating, as the compression is less rapid than with a perfect gas, and the product  $pv$  does not cease hereafter to increase.

(3) The more the temperature falls the more the initial fall of  $pv$  is accentuated and rapid (isotherms B, C, D . . .),



and, a fact indicated by Van der Waals' equation, the minimum of  $pv$ , which had commenced by being displaced towards the high pressures in the case of decreasing temperatures, is retrograding now progressively towards the feeble pressures as the temperature continues to lower (the

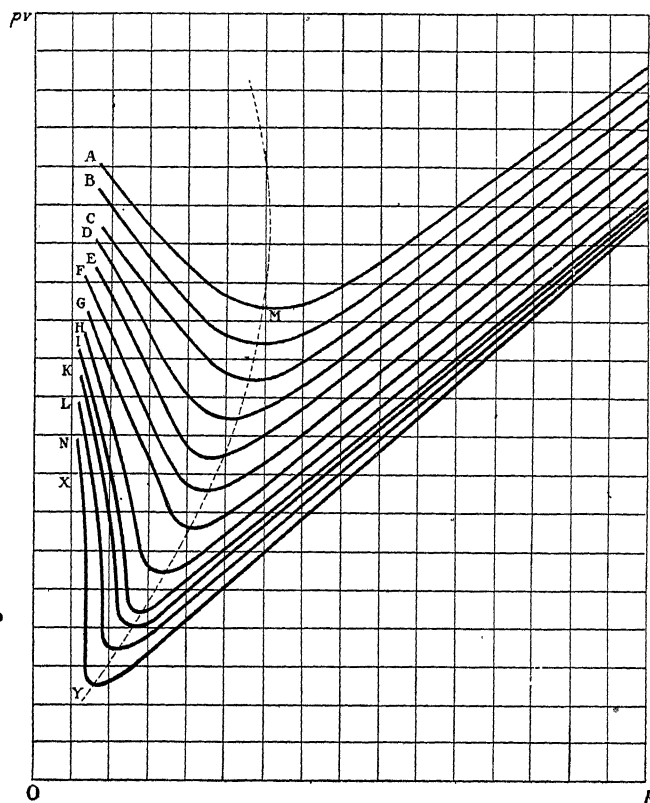


FIG. 38.

locus of the minimum of  $pv$  for the different isotherms is in point of fact a parabola, as the dotted line indicates in the figure).

We now reach the critical temperature (isotherme L). Here the fall of  $pv$  is so pronounced that the curve falls vertically at the moment of the critical pressure; this being passed  $pv$  ascends rapidly.

Finally, below the critical temperature we get at a certain pressure, the sudden liquefaction of the whole of the gas (p. 46), so that the curve  $x$  of  $p$  possesses a considerable vertical limb; beyond  $p$  it re-ascends with increasing rapidity, the liquid which is produced being very slightly compressible, so that the right-hand branch is practically a straight line,  $p$  being about doubled every time the pressure doubles. The generality of the figures constructed in this way constitutes what we call a *system*.

The curves of the preceding system are *ex hypothesi* constructed according to Van der Waals' formula. They simulate for each gas, let us repeat, the general appearance of the figures directly furnished by experiment.

We now reach a fact which is singularly interesting, which Van der Waals' equation revealed well ahead of experiment.

Van der Waals' equation, we have stated, applies to all gases, on condition that an adequate value be given to the co-efficients  $a$  and  $b$  for the gas under consideration determined by certain direct experiments.

This fact alone—that all the gases can be represented by a single form of equation—is already very suggestive; it presupposes necessarily, in the case of the isotherms of these different gases, a certain uniformity of behaviour. This is effectively, as we have just seen, what is demonstrated by the construction of the various figures, both by means of Van der Waals' formula and by the aid of the experimental results; doubtless at the same temperature, the singular gases, so variously removed from their respective points of ebullition, so different also in respect of their critical constants, cannot possess identical isotherms; but the analogy becomes self-evident provided we operate within sufficiently extended limits for each gas, and that the figures thus obtained be compared in their general features.

This first criticism of a general order had been already made by a number of physicists, but it had not satisfied Van der Waals.

Very often, it does not matter in what connection, the conclusions drawn from a certain order of facts vary essentially with the point of view at which we place ourselves; the aspect of a phenomenon depends upon the angle from which we look at it. It follows that a phenomenon, simple in itself, may seem indecipherable to anyone who does not know how to observe it in a proper way—and Nature probably only appears to us so often very complex, because we do not know how to refer it to a system of suitable co-ordinates.

Now Van der Waals, on the question of gases, encountered just such an experience. He had imagined that the general similarity of behaviour of the various figures might hide a deeper similarity, and if this were the case the similarity could not fail to appear through a suitable modification of the units used.

Experience has demonstrated the well-founded character of this happy thought. We have stated that Van der Waals' equation admits of facile calculation, not only of the numerical values, but of the analytical expressions themselves of the critical elements of the gases.

Well, let us measure the pressures, no longer in ordinary units, but by adopting as unit the pressure of the *critical pressure*  $P_c$ ; let us similarly measure the temperatures by taking as unit the absolute *critical temperature*  $T_c$ , and the volumes by taking as unit the *critical volume*  $V_c$ . Indicating by  $p_1, v_1, t_1$ , these new variables as thus defined, we have manifestly—

$$p_1 = \frac{p}{P_c}, \quad v_1 = \frac{v}{V_c}, \quad t_1 = \frac{t}{T_c},$$

or—

$$p = P_c p_1, \quad v = V_c v_1, \quad t = T_c t_1,$$

and if we replace  $P_c$ ,  $V_c$ ,  $T_c$  by their values (p. 116), viz.—

$$P_c = \frac{a}{27b^2}, \quad V_c = 3b, \quad T_c = \frac{8a}{27bR}.$$

we have—

$$p = \frac{ap_1}{27b^2}, \quad v = 3vr_1, \quad T = \frac{8at_1}{27bR}.$$

Let us substitute these values of  $p$ ,  $v$ ,  $T$  in Van der Waals equation—

$$\left( \frac{ap_1}{27b^2} + \frac{a}{9b^2v_1^2} \right) (3bv_1 - b) = \frac{8aRT_1}{27bR}.$$

or—

$$\frac{a}{27b^2} \left( p_1 + \frac{3}{v_1^2} \right) (3v_1 - 1) b = \frac{8aT_1}{27b}.$$

or finally—

$$\left( p_1 + \frac{3}{v_1^2} \right) (3v_1 - 1) = 8t_1.$$

This last equation is therefore the equivalent of Van der Waals' equation, but in which  $p_1$ ,  $v_1$ , and  $t_1$  are the pressures, volumes and temperatures, measured, as stated above, with the critical values as units of measurement. Now, the capital point to be observed is that in the equation thus obtained  $a$  and  $b$  have disappeared. Thus, the equation is quite independent of the values  $a$  and  $b$  peculiar to each gas. It results directly from this fact that this equation, which is called the *restricted Van der Waals*, is indiscriminately applicable to all gases, that is, on the condition that the systems are constructed for all the gases with the units we have just defined, these systems will be all identical!

In other words, on the condition of comparing the gases in corresponding states relatively to the critical condition, the properties of gases in respect of pressure, volume and temperature are identical.

At the time (1874) when Van der Waals enriched

science by his marvellous determination, as we have previously stated, the experimental data respecting gases were rather rare, and the verifications were both difficult and incomplete; but as soon as the work of physicists had filled up the gaps, Amagat was able to confirm the ideas of the illustrious scientific Dutchman in the most sensational

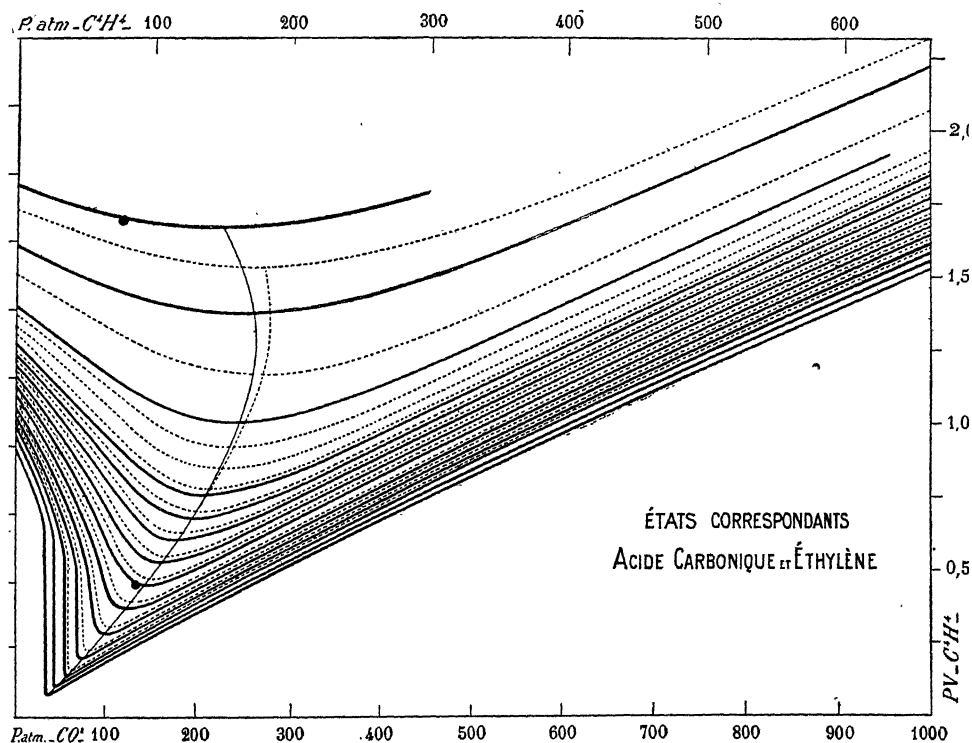


FIG. 39.—Superposition of the ethylene and carbonic acid systems according to Amagat.

way by graphically superposing the experimental systems, respectively brought and without any “faking” to suitable co-ordinates by a clever photographic device.

Fig. 39 shows the result of this superposition for the systems of carbonic acid and ethylene. Fig. 40, more striking still, shows the identity to be practically absolute for sulphuric ether, carbonic acid and air—that is, for three

and if we replace  $P_c$ ,  $V_c$ ,  $T_c$  by their values (p. 116), viz.—

$$P_c = \frac{a}{27b^2}, \quad V_c = 3b, \quad T_c = \frac{8a}{27bR},$$

we have—

$$p = \frac{ap_1}{27b^2}, \quad v = 3lv_1, \quad T = \frac{8aT_1}{27bR}.$$

Let us substitute these values of  $p$ ,  $v$ ,  $T$  in Van der Waals equation—

$$\left( \frac{ap_1}{27b^2} + \frac{a}{9b^2v_1^2} \right) (3lv_1 - b) = \frac{8a}{27bR} RT_1,$$

or—

$$\frac{a}{27b^2} \left( p_1 + \frac{3}{v_1^2} \right) (3v_1 - 1) b = \frac{8aT_1}{27b},$$

or finally—

$$\left( p_1 + \frac{3}{v_1^2} \right) (3v_1 - 1) = 8T_1.$$

This last equation is therefore the equivalent of Van der Waals' equation, but in which  $p_1$ ,  $v_1$ , and  $T_1$  are the pressures, volumes and temperatures, measured, as stated above, with the critical values as units of measurement. Now, the capital point to be observed is that in the equation thus obtained  $a$  and  $b$  have disappeared. Thus, the equation is quite independent of the values  $a$  and  $b$  peculiar to each gas. It results directly from this fact that this equation, which is called the *restricted Van der Waals*, is indiscriminately applicable to *all gases*, that is, on the condition that the systems are constructed for all the gases with the units we have just defined, these systems will be all identical!

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science by his marvellous determination, as we have previously stated, the experimental data respecting gases were rather rare, and the verifications were both difficult and incomplete; but as soon as the work of physicists had filled up the gaps, Amagat was able to confirm the ideas of the illustrious scientific Dutchman in the most sensational

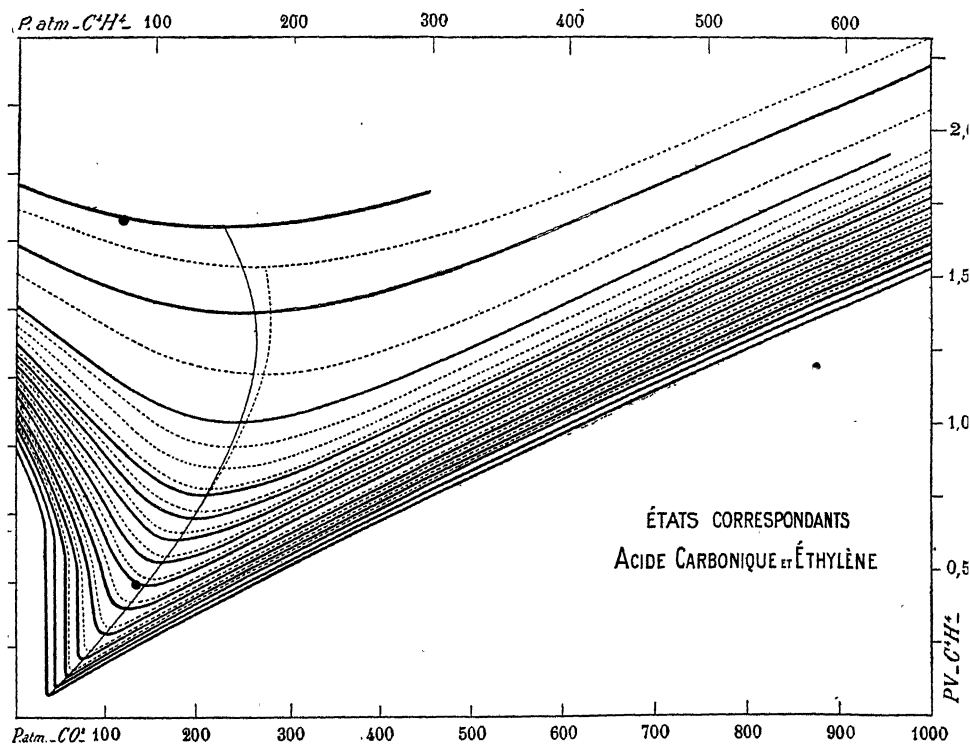


Fig. 39.—Superposition of the ethylene and carbonic acid systems according to Amagat.

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Fig. 39 shows the result of this superposition for the systems of carbonic acid and ethylene. Fig. 4, striking still, shows the identity to be practically for sulphuric ether, carbonic acid and air—that is,

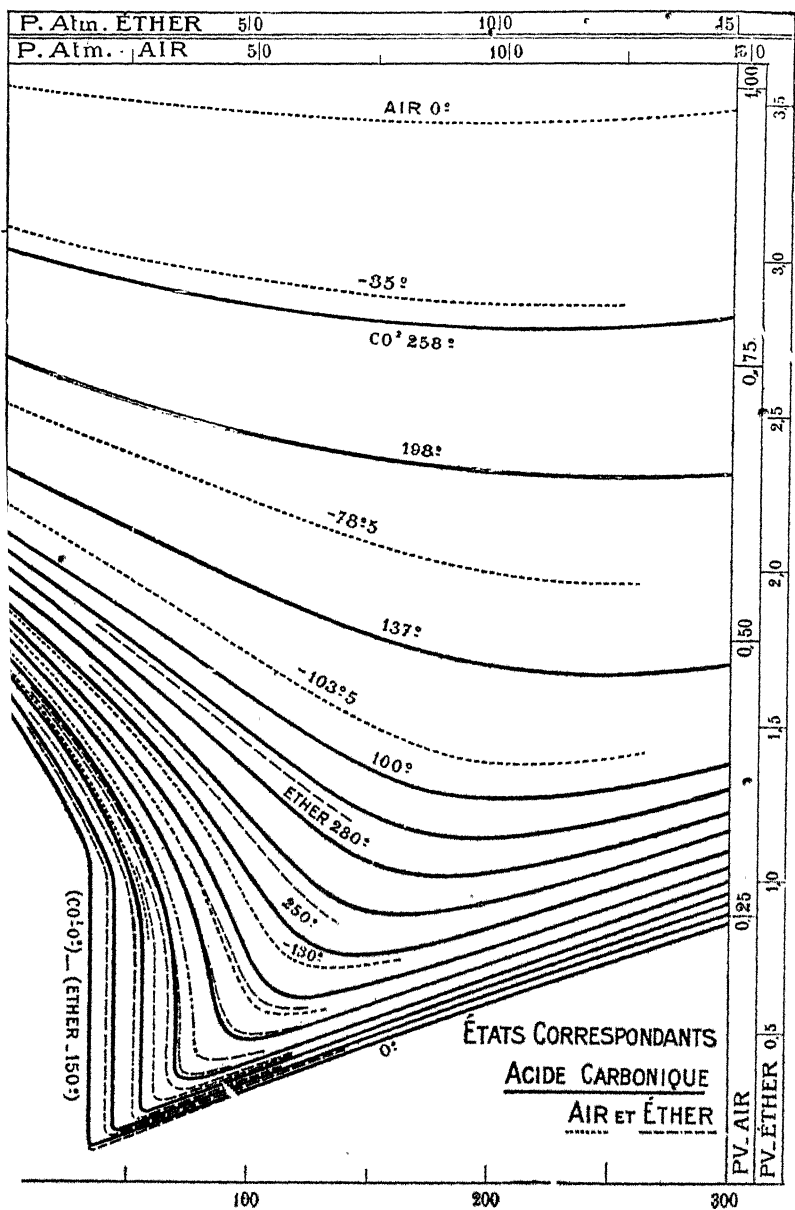


Fig. 40.—Superposition of the systems of carbonic acid, air and ether according to Amagat.



specimens which are about as different as possible in the series of fluids. •

Surprise may be felt at the perfection of the results obtained after the remarks we made as to the approximation involved in the Van der Waals' formula. It may be supposed, moreover, that the existence of an abbreviated variant independent of  $a$  and  $b$ , which is the reason itself of Van der Waals' conclusions, arises essentially from the form of the equation from which it is derived, and that another form of equation which should represent the facts more correctly might not admit of the possibility of such a variant. We may legitimately suppose this, but, in point of fact, the more exact formulæ of Clausius and Serrau (p. 116) admit, also, a variant, and all our conclusions persist. We could not either doubt this after the conclusive experimental confirmation contributed by Amagat, and we can now appreciate to what a dim past, the long triumphant idea of the permanent gases is now relegated.\*

#### COMPRESSIBILITY OF AIR AT LOW TEMPERATURES.

**Witkowski's work.**—The air system which we reproduced above was constructed by Amagat according to the results of a remarkable series of experiments carried out by Witkowski in 1891.† The whole physical history of the air is naturally inscribed therein, and correctly speaking we should not require to add anything thereto.

As, however, these results interest us more especially, we shall reproduce further on the table itself drawn up by the Polish scientist.

In his experiments a determined mass of air was submitted at constant temperature to progressively increasing

\* Certain experimental researches by Mathias, Berthelot, Mrs. Christine Mayer and a few other scientists have, however, to a small extent limited the general application of the preceding theories, which could not be exactly applicable save by the division of bodies into a certain number of groups.

† 'Bulletin of the Academy of Sciences of Crakow,' 1891.

pressures, and for each pressure the product  $p v$  of pressure by volume was measured with great precision. This series of measurements was recommenced for a second temperature, then for a third, etc. These experiments, in other words, furnished directly the elements of the successive isotherms of which we have been speaking above.

In Witkowski's experiments the mass of air experimented with, which was always the same, was such that the product  $p v$ , corresponding to  $0^{\circ}$  C. and 1 atmosphere, was precisely equal to unity. The following table is the exact reproduction of the results obtained. Furthermore, to facilitate subsequent calculations, the table on page 129 has been deduced from that for the case where the mass of air experimented with corresponds to the ordinary units for thermodynamic calculations, viz. 1 kilogramme of air, the pressure on its side being expressed in kilogrammes per square metre, that is on the scale of 10,333 kgs. per square meter and per atmosphere.

For the moment let us consider the first table: we find there, as a matter of course, the confirmation of our above conclusions, but its examination is not loss of time, it is essential that we should become familiar with the behaviour of air.

Let us first consider the series of measurements made at  $0^{\circ}$  C. If the air were a perfect gas we should get throughout the series  $p v = \text{a constant} = 1000$ . Now we find, on the contrary, from and after pressures of 10 atmospheres a slight curvature—nascent effect of the internal pressure—which is noticeable down to the minimum of 168, when a pressure of 95 atmospheres is attained.

As we see, this variation of  $p v$  which invalidates Mariotte's law is not very striking at ordinary temperatures, and shows that though air is not a perfect gas at these temperatures it is not far off it—at least with pressures under 150 atmospheres.

At temperatures over  $0^{\circ}\text{C.}$ , moreover, the excess of compressibility of air still decreases; at  $100^{\circ}\text{C.}$  it no longer exists, because Witkowski's table shows that the product  $pv$  increases at once slightly with the pressure.

Pressure in atmo- spheres.	$+100^{\circ}$	$+16^{\circ}$	$0^{\circ}$	$-35^{\circ}$	$-78^{\circ}$	$-103^{\circ}$	$-130^{\circ}$	$-135^{\circ}$	$-140^{\circ}$	$-145^{\circ}$
1	1.367	1.059	1.000	0.872	0.712	0.620	0.523	0.504	0.486	0.468
10	1.368	1.055	0.995	"	"	"	"	"	"	"
15	1.369	1.053	"	"	"	"	"	"	0.410	0.379
20	1.369	1.051	0.990	"	0.678	0.570	0.441	"	0.381	0.345
25	1.370	1.049	"	"	"	"	0.418	"	0.348	0.302
30	1.370	1.047	0.984	"	0.660	0.542	0.391	0.350	0.306	0.244*
35	1.371	1.045	"	"	"	"	"	0.312	0.242	"
40	1.373	1.043	0.979	"	0.642	0.513	0.333	0.260	0.113	"
45	1.374	1.042	"	"	"	"	"	0.194	"	"
50	1.375	1.041	0.975	0.829	0.625	0.484	0.254	0.1605	"	"
55	1.377	1.040	"	"	"	"	"	0.1553	"	"
60	1.378	1.039	0.971	0.822	0.609	0.457	0.201	0.1556	"	"
65	1.380	1.038	"	"	"	"	0.1985	0.1576	"	"
70	1.382	1.038	0.970	0.816	0.594	0.432	0.1985	"	"	"
75	1.384	1.0379	0.969	"	"	"	"	"	"	"
80	1.386	1.038	0.969	0.811	0.580	0.410	0.204	"	"	"
85	1.389	1.038	0.9682	"	"	"	"	"	"	"
90	1.391	1.038	0.9681	0.806	0.568	0.395	"	"	"	"
95	1.393	1.039	0.968	"	"	"	"	"	"	"
100	1.395	1.039	0.9681	0.802	0.560	0.388	"	"	"	"
105	1.398	1.040	0.9685	"	"	0.3874	"	"	"	"
110	1.400	1.041	0.969	0.8006	0.554	0.388	"	"	"	"
115	1.493	1.042	0.970	0.8004	0.553	0.389	"	"	"	"
120	1.496	1.043	0.971	0.8006	0.552	0.391	"	"	"	"
125	"	1.045	"	0.8012	0.553	0.394	"	"	"	"
130	"	1.047	0.974	"	0.553	0.398	"	"	"	"
Perfect gas	1.366	1.059	1.000	0.872	0.714	0.623	0.524	0.505	0.487	0.469

\* For 29 atmospheres.

At temperatures below  $0^{\circ}\text{C.}$ , on the contrary, the compressibility increases, revealing a rapidly augmenting imperfection of the gaseous state, or, to be more precise, a rapid increase in the effect of the internal pressure. At  $-35^{\circ}\text{C.}$  already,  $pv$  passes from 0.872, value at the commencement, to 0.800, minimum reached at 115 atmospheres.

At  $-103^{\circ}\text{C.}$  the effect becomes more noticeable still

$p_v$  passing from 0.620 to a minimum of 0.387 at 105 atmospheres. It becomes enormous at  $-140^\circ \text{C.}$ , where  $v$ , starting from 0.486, reaches 0.113 at 40 atmospheres. If we tried to apply to air under these conditions the formulæ of thermo-dynamics dealing with perfect gases, we should only make a mistake of about 300 per cent.! This extreme compressibility, this veritable giving way of the gas under the stress of pressure, makes us guess at the imminence of liquefaction, and we know in point of fact that  $-140^\circ \text{C.}$  is the critical temperature for air, and that at this temperature 50 atmospheres' pressure suffices to liquefy it.

Witkowski's table possesses another point of interest for us. It shows us clearly how compressed air behaves when circulating in a temperature exchanger and *being cooled under constant pressure* up to the orifice of expansion. It is sufficient for this to read the table, not vertically, but horizontally, along the line corresponding to the pressure employed. The anomaly of contraction, it is true, is here no longer so evident as in the vertical columns, because in gas, as it gets cooler, the product  $p_v$  would be diminishing even with a perfect gas. For this reason, as a standard of comparison, we have set down in the last line of the table, printed in *italics*, what would be, irrespective of pressure, these successive values of  $p_v$  for a perfect gas. The numbers for this line have been obtained by giving to the successive requisite values in the equation for perfect gases—

$$p_1 v_1 = p_0 v_0 \left(1 + \frac{t}{273}\right) = \frac{p_0 v_0 T}{273} = RT = 29.3T.$$

Thanks to this datum, we can see, by comparing with the horizontal line, the horizontal line corresponding to the selected pressure—100 atmospheres for example—how abnormally rapid, is the contraction of the air under this pressure at

the progressively lower temperatures met with in the exchanger.

We notice, moreover, the almost absolute identity of the supplementary line, relating to perfect gases, with the first line of the table, relating to the cooling of the air under atmospheric pressure. Some very slight differences certainly exist between the two lines, but these could be placed to the account of experimental errors, as they do not present any very systematic features. We can therefore say that, down to temperatures of  $-150^{\circ}$  C. at least, air behaves at atmospheric pressure very closely as a perfect gas, and we shall see (p. 141) the advantage we are going to take of this important fact.

Pressure in atmo- spheres	+ 100°	+ 16°	0°	- 35°	- 78°	- 103°	- 130°	- 135°	- 140°	- 145°
1	10936	8472	8000	6976	5696	4960	4184	4032	3888	3748
10	10944	8440	7960	"	"	"	"	"	"	"
15	10952	8424	"	"	"	"	"	"	3280	3032
20	10952	8408	7920	"	5424	4560	3528	"	3048	2760
25	10960	8392	"	"	"	"	3344	"	2784	2418
30	10960	8376	7872	"	5280	4336	3152	2800	2448	1952*
35	10968	8360	"	"	"	"	"	2496	1936	"
40	10984	8344	7832	"	5136	4104	2664	2080	904	"
45	10992	8366	"	"	"	"	"	1552	"	"
50	11000	8328	7800	6632	5000	3872	2032	1284·0	"	"
55	11016	8320	"	"	"	"	"	1242·4	"	"
60	11024	8312	7768	6576	4872	3656	1608	1244·8	"	"
65	11040	8304	"	"	"	"	"	1588·0	1260·8	"
70	11056	8304	7760	6528	4752	3456	1588·0	"	"	"
75	11072	8303·2	7752	"	"	"	"	"	"	"
80	11088	8304	7752	6488	4640	3280	1632	"	"	"
85	11112	8304	7745·6	"	"	"	"	"	"	"
90	11128	8304	7744·8	6448	4544	3160	"	"	"	"
95	11144	8312	7744·0	"	"	"	"	"	"	"
100	11160	8312	7744·8	6416	4480	3104	"	"	"	"
105	11184	8320	7748·0	"	"	3099·2	"	"	"	"
110	11200	8328	7752	6404·8	4432	3104	"	"	"	"
115	11224	8336	7760	6403·2	4424	3112	"	"	"	"
120	"	8344	7768	6404·8	4416	3128	"	"	"	"
125	"	8360	"	6409·6	4416	3154	"	"	"	"
130	"	8376	7792	"	4424	3186	"	"	"	"
Perfect gas	10928	8472	8000	6976	5712	4984	4192	4040	3896	3752

\* For 29 atmospheres.

The preceding is the same table, calculated for 1 kg. of air. Here, instead of making  $p_0 v_0$  at  $0^\circ \text{C.} = 1$ , we take—

$$v_0 = \frac{1 \text{ m}^3}{1.293} p_0 = 10,333 \text{ kg} : \text{m}^2,$$

$$p_0 v_0 = \frac{10,333}{1.293} = 7991,$$

or very approximately 8000.

The figures on this table have therefore been obtained by multiplying those of the preceding table by 8000.

## CHAPTER VI

## EXPANSION BY SIMPLE OUTFLOW

## ESTIMATE OF ITS OUTPUT.

WE can now explain to ourselves that which must take place in the expansion of real gases by simple outflow, and appreciate at their correct value the improvements with which Professor Linde has endowed this method.

For the sake of clearing our reasoning, instead of founding these, like the learned German, on the extrapolation of the Joule-Thompson formula, we shall take as starting-point Van der Waals' equation. Doubtless this starting-point will not be exempt from criticism, since this equation gives only an approximate representation of facts, but it will enable us at least to conceive an approximate representation of matters, while awaiting the more exact theories which physicists will doubtless offer us.

We will suppose, therefore, that the air complies with the relation—

$$\left(p + \frac{a}{v^2}\right) (v - b) = RT \text{ or } p = \frac{RT}{v - b} - \frac{a}{v^2};$$

$p$  is in this fashion the pressure applied on the gas,  $\frac{RT}{v - b}$  is the total pressure, the sum of the applied pressure and the internal pressure which acts on the gaseous molecules; finally  $\frac{a}{v^2}$  is that portion of this total pressure which constitutes the internal pressure.

**Compression of an imperfect gas.**—Let us isothermically compress the gas from  $p_0$  to  $p_1$ . The external work of compression,  $W$ , is as always  $\int p dv$ ;  $dv$  is negative, so—

$$W = - \int_{v_0}^{v_1} p dv = - \int_{v_0}^{v_1} \left( \frac{RT}{v-b} - \frac{a}{v^2} \right) dv,$$

or—

$$W = RT \operatorname{Log}_e \frac{v_0-b}{v_1-b} + a \frac{v_0-v_1}{b_0 v_1},$$

or approximately, by neglecting  $b$  and  $v_1$  compared with  $v_0$  which is allowable if we pass from one atmosphere to a high pressure,

$$W = RT \operatorname{Log}_e \frac{b_0}{v_1-b} - \frac{a}{v_1},$$

instead of—

$$W = RT \operatorname{Log}_e \frac{v_0}{v_1},$$

in the case of a perfect gas. To this external work of compression  $W$ , necessarily corresponds a development of heat  $W'$ .

424.

But this development of heat is not the only one which is produced by the compression of our real gas. There is another *which does not absorb any external work*, which is evolved at the expense solely of the internal energy of the gas, owing to the fact of the closing up of its molecules. In this respect, compression acts on a gas to a certain extent like liquefaction, and the internal heat which is exterminated thereby is furnished by a mechanism analagous to that which produces the heat of liquefaction.

Let us calculate this internal work of compression.

We have seen that the molecular attractions are to be translated by an internal pressure  $\frac{a}{v^2}$  which is added to the external pressure to bring about the compression of the gas—the internal work in question is manifestly measured by the work itself of the internal pressure, viz. :



$$W_1 = - \int_{v_0}^{v_1} \frac{a}{v^3} dv = \frac{a}{v_1} - \frac{a}{v_0}.$$

Let us represent this result graphically: let  $MN$  (Fig. 41) be the curve of internal pressure  $\frac{a}{v^3}$  as a function of its volume. The work effected by this internal pressure between the two volumes  $v_0$  and  $v_1$  is clearly represented by the area subtended by the curve between these two volumes.

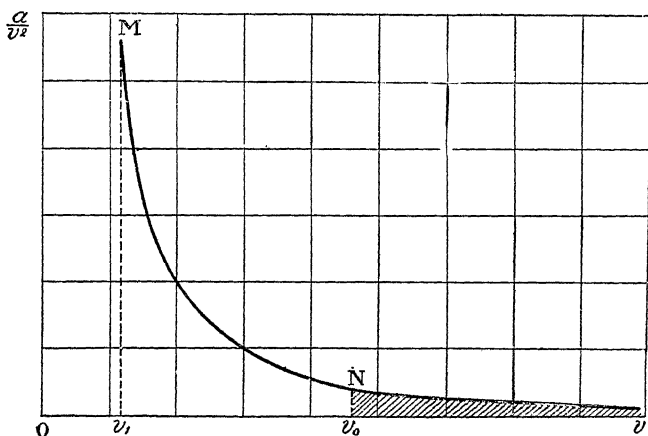


Fig. 41.—Heat subtracted during compression by the internal work.

This area is the difference between the total area extending from infinity down to  $v_1$ , which equals  $\frac{a}{v_1}$  and the area from infinity up to  $v_0$  which equals  $\frac{a}{v_0}$ , that is to say, the work  $\frac{a}{v_0}$  (represented by the hatched portion) which would be expended by the internal pressure, from infinity to  $v_0$ , is small, and that we shall have closely—

$$W_1 = \frac{a}{v_1}.$$

On the whole, the liberation of heat corresponding to the compression of a real gas is therefore—

$$\frac{W + W_1}{424} = \frac{1}{424} \left[ RT \log \frac{v_0}{v_1 - b} - \frac{a}{v_1} + \frac{a}{v_1} \right] = \frac{1}{424} RT \log \frac{v_0}{v_1 - b},$$
 instead of—

$$\frac{1}{424} RT \log \frac{v_0}{v_1}$$

for a perfect gas.

For air the co-efficient  $a$  in the equation of Van der Waals, is sensibly equal to 12; if we compress it from 1 to 200 atmospheres, which is the case in the Hampson process, we have on the other hand—

$$V_1 = \frac{1}{1.293 \times 200} = 0.00387$$

(at this pressure, in fact,  $pv$  with air is very closely equal to  $p_0 v_0$ ).

We extract, therefore, per kilogramme of air in the cooling water of the compressor owing to the *internal* work during compression :

$$\frac{a}{v_1} = \frac{12}{0.00387} = 3100 \text{ kgms., or } 7.3 \text{ kilotherms.}$$

#### Expansion by simple outflow of an imperfect gas.—

Let us now expand by simple outflow from  $p_1$  to  $p_0$  the gas which we have just been compressing. During the compression the internal pressure provoked a notable evolution of heat, analogous to the heat of liquefaction. During expansion the contrary effect will be produced, involving an absorption of heat comparable to that caused by volatilisation, and this effect as a source of cold will superpose itself on the other different effects which may be produced.

As we have to deal in this kind of expansion with a continuous outflow, we have to take into account besides the energy pertaining to the air which is expanded, the energy transmitted by the compressor in the form of work in rust.\*

\* We cannot, on the contrary, neglect the kinetic energy of the jet; whether we arrange as in the Joule-Thomson experiment so that the velocity of the jet should be practically negligible, or that we estimate this kinetic energy, directly destroyed doing away with the velocity, hardly alters matters otherwise than by an absorption of heat immediately followed by its restitution.

It will suffice for us, on the other hand, to supplement the reasoning on page 104, so as to take into account the gaseous imperfections of the air.

(1) We will suppose to start with, that no exchanger is interposed between the compressor and the expander. The energy directly led from the compressor through the pipes equals as always  $p_1v_1$ .

If the initial pressure  $p_1$  is close to or not far removed from the pressure which produces the minimum  $p_v$  we have, according to Witkowski's table  $p_1v_1 < p_0v_0$ .

According to our reasoning (p. 104) this is the necessary course of cooling; if this effect alone was in question the expansion would itself be essentially expansion with external work. But this effect is invariably extremely feeble, since, according to Witkowski's second table (p. 127), between the minimum itself  $p_v$  at  $0^\circ$  C., corresponding to  $p_1 = 95$  atmospheres and  $p_0v_0$  corresponding to  $p_0 = 1$  atmosphere, we only obtain per kilogramme of air—

$$p_0v_0 - p_1v_1 = 256 \text{ kgms., or } 0.6 \text{ kilotherms;}$$

even then the fall in temperature amounts to  $\frac{0.6}{0.17} = 3.5^\circ$  C.

in all, or  $0.036^\circ$  per atmosphere; that is about *one eighth* of what is actually found by the Jules-Thomson experiment. It would be vain to contend that this effect (the inferiority of  $p_1v_1$  as compared with  $p_0v_0$ ) must be considerably increased at the very low temperature of expansion, as we shall see (p. 144) that the real frigorific efficiency depends solely on the gaseous imperfection at the temperature of admission to the exchanger.

It is necessary besides that we should count upon quite another circumstance in expansion by simple outflow, since we compress the air to such an extent, viz. to 200 atmospheres, that  $p_1v_1$  has passed the minimum and has become once more sensibly equal to  $p_0v_0$ , so that the slight frigorific gain that we might have hoped for through

operating close to the *pr* minimum does not even exist in this case.

We shall see, in point of fact, that the preponderating factor is agreeable with Linde's indications and contrary to the opinion of Pictet,\* the internal work.

To enable us to understand the matter let us recall that we have found that during compression the internal energy of the gas diminishes by  $\frac{u}{v_1}$  owing to the fact of the evolution of heat caused by the molecules being made to approach closer. Inversely, when a gas is expanded, neglecting all external work, a spontaneous cooling action takes place in the gas itself, which corresponds to the internal work accomplished by the molecules; this cooling must be produced, we presume, whatever the conditions of the expansion may be,† and more especially when the expansion is effected by simple outflow.‡

Let us calculate this internal work of expansion.

As above, it is sufficient to consider (Fig. 42) the curve of internal pressure  $\frac{u}{v^2}$  as a function of the volume.

Although the expansion is adiabatic and no longer isothermic, this curve is the same for expansion as for compression, since the internal pressure in the Van der Waals formula is only a function of the volume alone.

\* "The preceding point is important, and shows very well that Linde's machine only produces liquid air by means of the external work and in no way because of any internal work whatever (!)" (Pictet's work referred to—'Die Theorie des Apparate,' pp. 56 and 57).

† In the case of hydrogen, however, *heating* occurs in expansion of this kind. This fact, which appears to conflict with theory, furnishes on the contrary the best proof of its exactitude, because in the case of hydrogen at the temperature of the environment, the internal pressure is very slight, therefore the internal work done is very slight, while the corresponding volume is approximately equal to that of other gases, and consequently the term  $p_1v_1$  is much greater than  $p_0v_0$ , which is clearly a cause of heating.

‡ In expansion with external work, the cooling due to the internal work is added, it is understood, to that resulting from the external work. But the pressures involved being in this case very slight, this gain is hardly appreciable—5 per cent. (out) in the Claude machines.

The work produced equals always the area  $\frac{a}{v_1} - \frac{a}{v_0}$  subtended by the curve between the initial volume  $v_1$  and the final volume  $v_0$ ; the only difference being that the latter is not quite equal to the volume  $v_0$  from which we started in compression, because of the fall in temperature due to the expansion. The internal work during expansion is therefore, lessened by the hatched portion, but we can see how very slight is this diminution under our hypothesis when  $v_0$  is great, in comparison to  $v_1$ . If, for example,  $v_0$  is

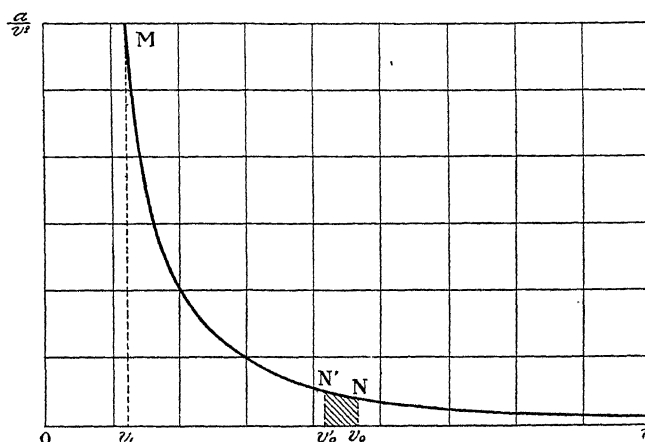


FIG. 42.—Heat absorbed during expansion by the internal work.

ten times less than  $v_1$  the ordinate  $Nv_0$  is a hundred times less than  $Mv_1$ ; the hatched portion is, therefore, very small and we can neglect  $\frac{a}{v'_0}$  on the same grounds as  $\frac{a}{v_0}$ , and assume that the internal work produced by the expansion is practically equal to  $\frac{a}{v_1}$ , like the internal work during compression.

We see in this way the essential difference between the internal and external work; the quantity of heat given off by external work does not correspond to cold when

expansion takes place save to the extent of the counter-pressure opposed to this expansion; the giving off of internal heat when compression takes place, on the contrary, involves necessarily on expansion, a sensibly equivalent shortage of heat, since under the sole condition that  $v_0$  is large in comparison with  $v_1$ , this work only sensibly depends on the volume  $v_1$  to which we have reduced the gas before expansion.

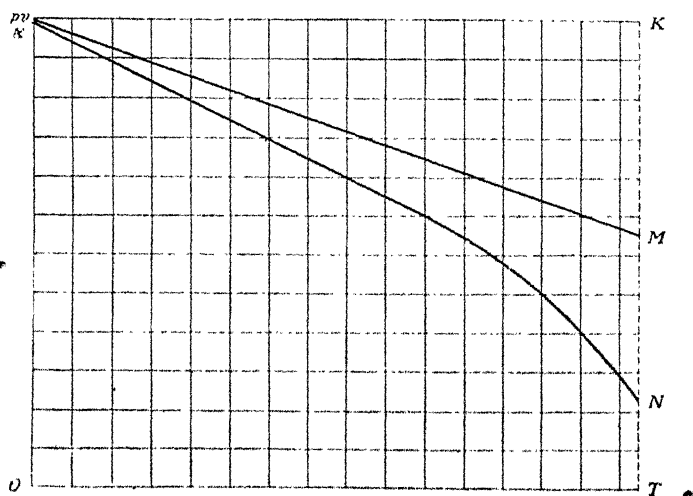


FIG. 43.—Diminution of  $pv$  in compressed air through cooling.

To resume: agreeably with Linde's assertion, the frigorific effect in this method of expansion is indeed essentially the effect of the *internal work* <sup>*at*</sup>  $v_1$ .

(2) **Expansion is effected after an exchanger of temperatures.**—We have to see now the extent to which our conclusions are modified by the fact that in liquid air appliances, the expansion of the compressed air, is not effected immediately after its compression, but after it has passed through an exchanger of temperatures where it is actually cooled in its passage in the contrary direction to

the expanded air. It is certain that this cooling brings it to a condition where its imperfections are largely increased, which is calculated at first sight, to greatly modify the conclusions to be drawn from a method which exclusively depends on this imperfection. We shall, however, see that the frigorific efficiency, in spite of appearances, is essentially dependent upon the gaseous imperfection at the temperature of *entry* of the compressed air into the exchanger, and that it is still the heat which we have succeeded in extracting at this temperature through the work of internal pressure which accounts for the whole.

The compressed air passing through the exchanger is cooled under constant pressure up to the expansion outlet. If it were a perfect gas it would contract indefinitely, by  $\frac{1}{273}$  part of its volume at  $0^{\circ}\text{C}$ . for each degree, and its heat capacity would remain constant. But it is not perfect. To see how it behaves it would be necessary, as we have explained (p. 128), to follow the horizontal line in Witkowski's table relating to the pressure in question; but this table, which is limited to 130 atmospheres, does not extend far enough, since we are operating at 200 atmospheres in the apparatus which is founded on this method of expansion.

We can, however, see how matters are at this pressure, by comparing Witkowski's table with Amagat's experiments at the ordinary temperature.

The behaviour is indicated by the curve  $AN$  (Fig. 43). Starting from the temperature of the environment with a  $pv$  differing very slightly from  $AO$  that, of a perfect gas, the gas in question reaches  $T'$  with its  $pv$  reduced, not to  $MT'$  as in a perfect gas, but to  $NT'$  only.

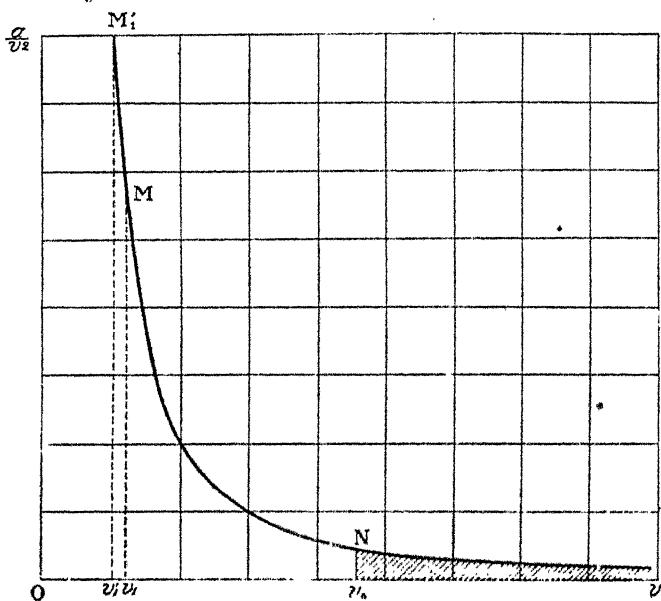
What is the reason for this first result?

Firstly, the air which is cooled, while contracting under constant pressure through the thrust of the air that follows, receives external work (furnished by the compressor)—

$$\int p \, dv = p \int dv = p \, \Delta v = KN,$$

work transformed into heat which exceeds by  $MN$  what it would receive if it were a perfect gas. It gives, out therefore, because of this, and communicates to the expanded air in its passage through the exchanger, the heat equivalent of  $MN$ , in addition to that which would be given out by a perfect gas while descending to the same temperature  $T$ .

Secondly, on the other hand, the contraction from  $v_1$  to



g. 44.--The quantity of heat  $MNv_1v_2$  subtracted by the internal work during compression is increased to  $MNv_1v'_1$  during the passage through the exchanger.

is accompanied by another evolution of additional heat, milarly received by the expanded air and corresponding the internal work, *i.e.*, the work inherent in the molecular traction; this work represented by the area  $MM'v_1v'_1$  (fig. 44) is the greater, in that in this portion of the cycle e internal pressure increases enormously through the st of contraction itself.

These two abnormal evolutions of heat 1 and 2, due to seous imperfection of air, must be accounted for by a



*progressive increase of the specific heat of the compressed air during cooling.*

It is, in fact, what has been established experimentally, and the following table, drawn up by Linde, shows also the extreme importance of the variations in the specific heat of air strongly compressed as a function of its temperature.

Temperature.	1 atmosphere.	10 atmospheres.	20 atmospheres.	40 atmospheres.	70 atmospheres.	100 atmospheres.
100°	0·237	0·239	0·240	0·245	0·250	0·258
0°	0·238	0·242	0·247	0·251	0·277	0·298
— 50°	0·238	0·246	0·257	0·279	0·332	0·412
— 100°	0·239	0·259	0·285	0·370	0·846	—
— 150°	0·240	0·311	0·505	—	—	—

Now what is going to take place when the gas is expanded down to atmospheric pressure?

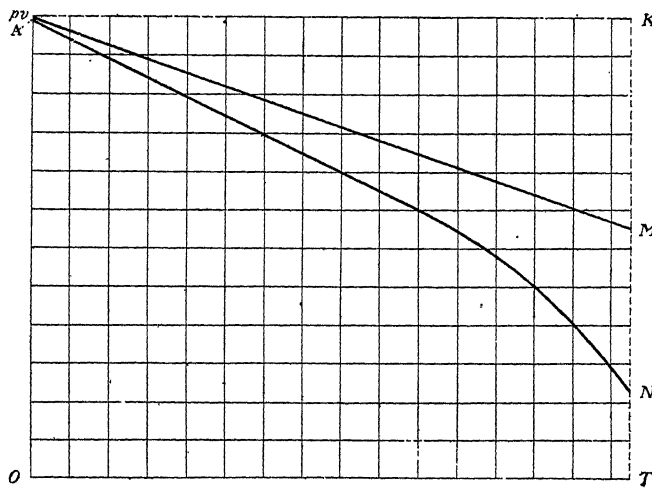


FIG. 45.—Increase of  $pv$  of compressed cooled air on expansion.

We know, according to Witkowski (p. 128), and according to the preceding table, that the expanded gas recovers very sensibly under the atmospheric pressure the conditions of a perfect gas.

The  $pv$  of this air, reduced to  $NT$  (Fig. 45) by the effect

of the anomalies of contraction, would recover after expansion, if the temperature  $T$  is unchanged, a value  $MT$ , equal to that of the perfect gas through performing against  $p=1$  atmosphere a work of accumulation exactly equal to its new  $pv$ , viz.  $MT$  (see the reasoning, p. 104). The work of thrust transmitted from the compressor to the expansion outlet corresponding only to  $pv$  in compression, to wit  $NT$ , there would result therefrom, at the moment of expansion of the air, an absorption of heat equivalent to  $MT-NT=MN$ , that is *precisely equivalent* to the heat abnormally evolved in the exchanger by the fact of the work of thrust.

This absorption of heat would therefore quite simplify the effect of placing the expanded air in a condition to take up, notwithstanding its inferior frigorific capacity, the excess of heat  $MN$  developed all along the exchanger by the succeeding compressed air.

It would be simply a case of borrowing what is returned and not corresponding to *any real frigorific effect*; the only cold which counts, we can understand, is that which is produced outside of any countervailing heat destined to neutralise it, which is evidently not the case with that which corresponds to  $MN$ .

The preceding supposition that the temperature does not fall at the moment of expansion is, on the other hand, absurd, because in the adiabatic expansion it is only cooling which cannot be translated, by the transformation of heat, into work.

Consequently the work of recompression in the case of expansion is less than  $MT$ , its excess over  $NT$  is less than  $IT$ , and the immediate cooling only compensates for a part of the excess of heat  $MN$  evolved in the process. But this deficit is made good by the increase of volume of the expanded air between the temperature  $T''$  of the end of the expansion and that of  $T$  at the commencement, during which completes exactly its  $pv$  at  $MT$ , at the expense of taking

up an equivalent amount of heat; beyond  $T$  at the temperature of the environment, because it is a gas which is sensibly perfect, its work of expansion  $KM$  is exactly equal to the "normal" portion of the heat evolved during the first stage through the contraction of the compressed gas. The whole work of re-compression and of expansion is thus exactly equal to  $KT$  that is the outside energy  $p_1v_1$  furnished by the compressor.

Therefore in this case also, the external work does not count from the point of view of cold, and the internal work has to accomplish the whole operation alone.

Now, how does the air behave during expansion in respect of this internal work?

At the moment when it reaches the orifice of expansion we know that it has lost, because of the work of internal pressure, a first quantity of energy  $\frac{a}{v_1}$ , viz.  $MNv_0v_1$  (Fig. 46), which has disappeared in the injection water of the compressor, and a second quantity  $\frac{a}{v'_1} - \frac{a}{v_1}$ , viz.  $MM'v_1v'_1$ , which is liberated and parted with, to the air expanded in the exchanger in proportion to the cooling. At the moment of expansion, work in the contrary direction to the internal pressure, work of increase of volume, is produced and involves a cooling of the expanded air.

As in the preceding case, this internal work during expansion may be shown by constructing the curve of the internal pressure as a function of the volume (Fig. 46), and by estimating the area subtended by this curve between the initial and final volumes.

The initial volume is nothing else than the final volume compressed and cooled of the previous case, viz.  $v'_1$ , and the internal work of expansion is, consequently, exactly equal and of contrary sign to the internal work of compression and cooling, and the pressure  $\frac{a}{v'}$  to the extent

that the expanded air at  $p_0$ , because of its being cooled, regains only the volume  $v'_0$  considerably less than the initial volume  $v_0$ . Hence a slight loss arises  $NN'r'_0$  in the

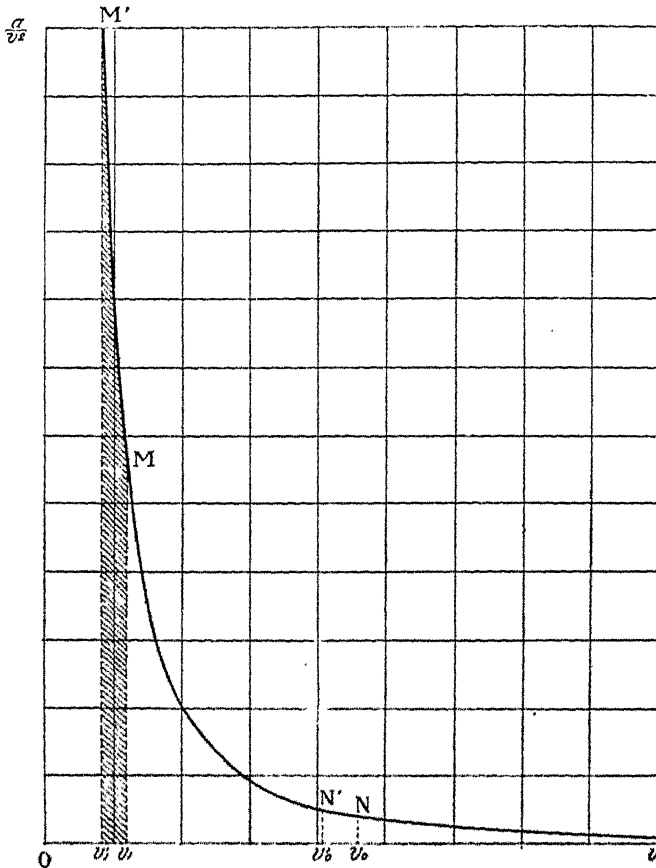


FIG. 46.—Variations in the internal work during compression, cooling and expansion.

cooling at the instant of expansion. But this loss will make itself good during the passage of the expanded air through the exchanger on its reverting to the temperature of the environment and consequently to the volume  $v_0$ . Generally the quantity of cold which is produced by the fact of the internal work during and after expansion, is *exactly equal* to the quantity of heat evolved previously.

Of this production of cold  $\frac{u}{v_1}$ , or  $M'Nv_0v_1$ , a portion,  $M'Mv_1v'_1$  evidently does not count in the real frigorific yield, and simply serves, on the same footing as the cold produced by the increase of  $pv$  during expansion, to furnish to the expanded air a supplementary cooling, serving to absorb the heat  $M'Mv_1v'_1$ , evolved by the internal work of contraction in the exchanger. *The excess  $MNv_1v_0$ , counts only against the frigorific yield and will be represented by liquid air, and will be found thus to be precisely equal to the quantity of heat evolved through the fact of internal work before entry into the exchanger.*

Thus a very important result, and one already suspected (p. 137), is reached, that whatever may be the nature of expansion, and, so to say, whatever may be its temperature, the internal work of expansion, in contra-distinction to external work, is neither diminished nor increased by the fact of cooling, and produces a useful frigorific effect sensibly equal to the inverse calorific effect at the temperature of compression.

This remarkable conclusion is naturally true to the degree of approximation of Van der Waals' hypothesis, according to which the internal pressure only depends upon the volume; neither does it take into account the small amount of air which is liquefied.\*

**The fall in temperature at expansion furnishes a fictitious and exaggerated value of the frigorific effect.**—In this way, for the portion which relates to the internal work, as well as the external work of contraction, the

\* We have not taken into account in our reasoning, of the heat of cooling properly so called, of the gaseous molecules themselves which correspond with the specific heat at the constant volume  $c$ . It is very possible that this specific heat does not alter with the temperature and the pressure; on the other hand, independent of any hypothesis on the point, we could show, as we have done for  $pv$ , that the only definite effect of a possible variation, would be limited to that of the difference, which is wholly negligible, of the values of  $c$  under the pressure of 200 and of 1 atmosphere at the temperature of the inlet.

increase in the gaseous imperfections in the exchanger during cooling, and the abnormal evolution of heat which arises therefrom, do not count from the point of view of the cold-producing yield.

This amounts to saying that the fall in temperature determined at expansion, furnishes an entirely erroneous idea of the real frigorific yield; beside a fixed amount which corresponds to this real yield is included a *fictitious amount*, which is the larger the lower the temperature, and is destined to endow the expanded air, in spite of its lower calorific capacity, with the means of retaining the heat abnormally evolved during the cooling of the compressed air.

It is, therefore, wholly false, as many superficial commentators of the Joule-Thomson formula are pleased to assert, that the efficiency of expansion with internal work is rapidly self-increasing when the temperature falls, and it is one of Linde's great merits, that he should have perceived this.

Linde's merit, which is solid for quite other reasons, is precisely for having quite clearly perceived, that this efficiency, such as it is, amounted to very little, and for having indicating some very clear means of increasing it.

Let us repeat, the only thing which accounts for the real yield is the gaseous imperfection *at the temperature of admission* to the exchanger—that is, the temperature corresponding to the heat  $\frac{u}{v_1}$  is effectively and definitely eliminated from the system.

**Improvements introduced by Linde in expansion with internal work.**—The above reasoning, which is inevitably insufficiently elaborated, will at least enable us to at once understand the conclusions to which we are going to be led.

We believe, in point of fact, that the essential objective

to aim at, should be to increase as much as possible *for a given amount of work* the quantity  $\frac{a}{v_1}$  expelled from the compressed air by the internal work before its entrance into the exchanger.

Now,  $a$ , the co-efficient of Van der Waals' equation, is intangible; it is for air sensibly equal to 12; and we can only act upon  $v_1$ .

Whence arise the two improvements indicated by Linde?

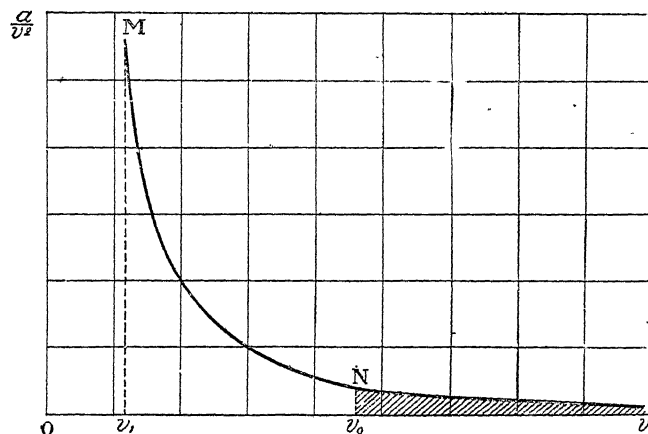


FIG. 47.—Uselessness of pushing expansion very far to benefit the internal work.

First, so that  $\frac{a}{v_1}$  shall be of appreciable value,  $v_1$  must be very small.

The process stands therefore condemned at very high pressures, and the deficiency seems to be irreparable from the point of view of economy.

Linde has got round the difficulty in a very ingenious fashion. This work of the internal pressure, in point of fact, only depends, at the degree of approximation with which we operate, on the initial pressure. We shall not diminish it (or at least not sensibly) if we do not expand down to atmospheric pressure. It is sufficient, we have remarked,

that  $v_0$  after expansion shall be large enough, compared with  $v_1$  (five to ten times for example), for the quantity of cold  $\frac{v_1}{v_0}$  to be very sensibly increased, since only the hatched surface to the right of Fig. 47 is in question, which, extended to infinity, is equal to  $\frac{v_1}{v_0}$ .

Now it is of the first importance to stop the expansion at a pressure  $p_0$  which is still considerably elevated.

In point of fact, during expansion, a very small portion of the air, about 10 per cent., is liquefied. All the remainder, on issuing from the exchanger, may be recuperated, recompressed, and returned to the cycle of operations. This would be wholly devoid of interest if this air had been reduced to atmospheric pressure and had to be wholly recompressed to return to the cycle; it is, on the contrary, of very great importance if the air has only been expanded down to a pressure  $p_0$ , which is much higher than atmospheric pressure, because the work of compression of each kilogramme of air is, as is well known, proportional to  $\text{Log} \frac{p_1}{p_0}$ , and diminishes considerably as  $p_0$  approaches  $p_1$ . If for example, we expand from 200 down to 1 atmosphere as with Hampson's method, the work of compression is proportional to  $\text{Log} \frac{200}{1}$ , viz. to 2.30; Linde, on the contrary, by expanding from 200 down to 50, proportions the work expended, to  $\text{Log} \frac{200}{50}$ , or only to 0.60, while only reducing the frigorific effect by one quarter. This shows the very great interest of this clever artifice.

We should not, however, omit from this reasoning the volume of atmospheric air required to replace the liquefied portion—to wit, some 10 per cent.; thus the gain pointed out above only affects some nine tenths of the air treated.



Second, the utilisation of a certain initial pressure being permitted, the quantity of heat *usefully* expelled from the gas through internal work will be augmented, and consequently the frigorific yield, through *cooling* the gas after its compression also so as to diminish  $v_1$  and increase  $\frac{a}{v_1}$ .

This is the very clever foundation for Linde's auxiliary cold-producing machine (p. 91).

We furthermore, in this way, profitably obtain heat from the gas through the fact of the diminution of  $pv$ , because at 200 atmospheres and at  $-50^\circ$  C.,  $pv$  is smaller than  $p_1v_1$  by about 400 kilogrammeter kilogrammes, and the total cycle of contraction and of dilatation of the air will be balanced without these 400 kilogrammeters, whence a supplementary gain of 1 calorie kilogramme.

At first sight the use of this auxillary cold-producing machine takes on the rather disconcerting appearance of the "fifth wheel of a coach," this, however, only increases the merit of its conception. We acknowledge that we were at some pains to understand the part it played. It seemed somewhat puerile to cool the compressed air down to  $-50^\circ$  C. by certain subsidiary and complex means, which by its passage through the exchangers would very simply cool itself down to  $-130^\circ$  or  $-140^\circ$  C. But we now understand all the necessity for the device, since we know that all the calories extracted in the course of cooling in the exchanger owing to the fact of internal work do not contribute to our objective, and that the real frigorific effect is that which corresponds to the temperature of admission to the exchanger. This frigorific effect will thus be increased through the auxiliary cooling by the whole amount of  $MM_1v''_1v_1$  (Fig. 48) gained from the area  $MM'v'_1v_1$  subtended by the curve (Fig. 46) which was effectively lost to us.

This conception was all the more reasonable and all the

more happy since the auxiliary frigorific machine produced its degrees of cold very economically down to  $-56^{\circ}\text{C}$ . (at the rate of 800 to 1000 per h.p. hour). Besides, it is manifest that this machine did not play the part of a substitute by

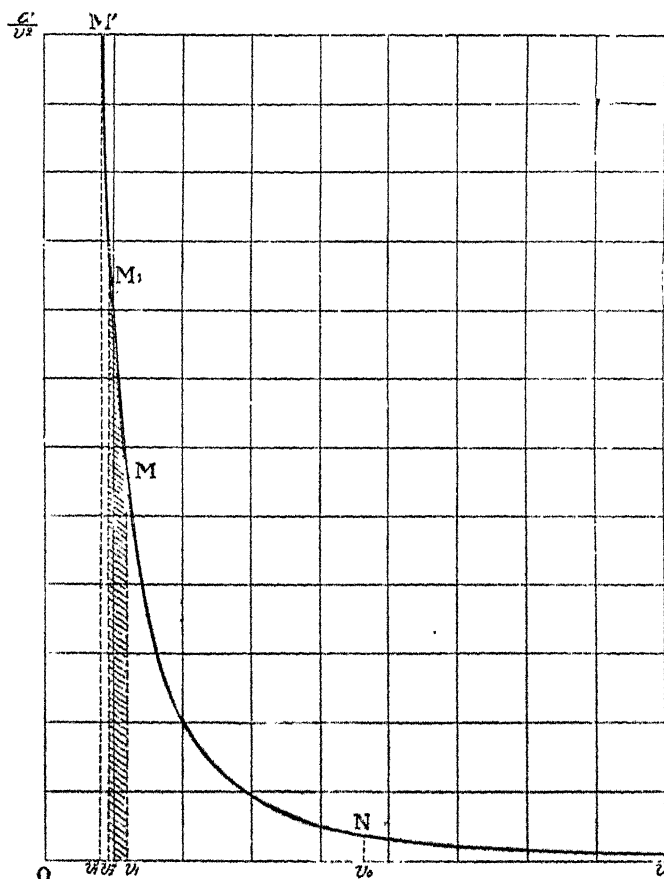


FIG. 48. — Gain obtained by auxiliary cooling.

itself for expanded air to cool the compressed air from the temperature of the environment down to  $-50^{\circ}\text{C}$ ., and would have involved the loss of the cold of the expanded air, which would thus have escaped from apparatus at  $-50^{\circ}\text{C}$ . The part played by the auxiliary machine is, a point of fact, simply to supplement the calorific in-

sufficiency of the expanded air when taking up the excess of heat evolved by the compressed air, and it ensures cooling *concurrently* with it, as the diagram in Fig. 31 shows.

**Frigorific value of Linde's expansion.**—We have now to assign numerical values to the preceding formulas.

We have stated that in Van der Waals' equation  $a$  is sensibly equal to 12 for air;  $v_1$  is, on the other hand, the volume in cubic metres of 1 kilogramme of air under the pressure of 200 atmospheres.

At this pressure and at  $0^\circ$  C. we have—

$$V_1 = \frac{1}{10,330 \times 200} = 0.00387.$$

Both expansion and compression are effected by Linde between 200 and 50 atmospheres, so we may not any longer neglect  $\frac{a}{v_0}$ , which is in fact sensibly equal to a quarter of  $\frac{a}{v_1}$ .

The internal work removed between 50 and 200 atmospheres at  $0^\circ$  C. is thus for each kilogram of air—

$$\left(\frac{a}{v_1} - \frac{a}{v_0}\right) = \frac{3}{4} \frac{12}{0.00387} = 2400 \text{ kilogrammeters, or } 5.7 \text{ calorie kilogrammes.}$$

At  $-50^\circ$  C., or  $223^\circ$  absolute temperature, the internal work removed between 50 and 200 atmospheres will become very closely—

$$\left(\frac{a}{v_1} - \frac{a}{v_0}\right) \frac{273}{223} = 2950 \text{ kilogrammeters, or } 7 \text{ calorie kilogrammes,}$$

and the gain due to the supplementary cooling will be increased by yet 1 calorie kilogramme through the fact that at this temperature the  $pv$  of the air is less than the corresponding  $p_0v_0$  by about 400 kilogram meters, gained through the cooling effect in accordance with what we have determined. There is therefore a total theoretic gain of 2.3

calories compared with 5.7, viz. 40 per cent., which is added by the supplementary cooling.

On the other hand, we must admit that in the Linde apparatus of the air treated there is about 10 per cent. which is liquefied (half of which is evaporated when the pressure falls), so that nine tenths of the air is compressed from 50 to 200 atmospheres and one tenth from 1 to 200.

Let us see what is the cost under these circumstances of compressing 1 kgm. of air. We can, under these conditions of pressure and temperature, apply without sensible error the ordinary formulas—

$$W = 0.9 p_0 v_0 \text{ Log. } \frac{200}{50} + 0.1 p' v' \text{ Log. } \frac{200}{1}.$$

With air we get very approximately  $p_0 v_0$  or  $p' v' = 8000$ . Therefore—

$$W = 7200 \text{ Log } 4 + 800 \text{ Log. } 200 = 9940 + 4250 = 14190 \text{ kgms.}$$

If we admit for the compressors a yield of two-thirds of the theoretical yield, we see that it is possible to compress in practice, per h.p. hour, under the assumed conditions—

$$\frac{270,000}{14,190} \times \frac{2}{3} = 12.7 \text{ kgms. of air.}$$

The total cold produced during expansion being theoretically equal for each kilogramme to the  $7 + 1 = 8$  calories previously found, it appears that the total theoretical frigorific yield\* is  $8 \times 12.7$ , or very nearly 100 *calories per h.p. hour*, and about 90 if the expenditure of energy be taken into account required for the cold-producing machine. This agrees perfectly with the *practical* yield of 0.61, or about 60 calories per h.p. hour, realised in the large Linde apparatus. Without Linde's two improvements, the yield of the expansion between 200 and 1 atmospheres, that is, the yield of Hampson's expansion, would simply amount 0—

$$\frac{12}{0.00387} = 3100 \text{ kgms. or } 7.3 \text{ calorie kilogrammes.}$$

\* Starting from the practical yield of the compressors, it is always in this sense that we shall speak of the theoretical yield.

or, for the 4 kgms. of air which we are able in practice to compress per h.p. hour from 1 to 200 atmospheres, or 30 calories only.

In this way Linde's improvements have tripled the efficiency of this method of expansion.

**Possibility of further improvement.**—The question may be asked whether the limits of working within which Professor Linde operates are the best possible.

It would be very tempting *à priori* to still further increase the internal work  $\frac{a}{v_1}$  by working at still higher pressures, because the laws of compression offer every scope in this direction, since the compression of air between 125 and 500 atmospheres, for instance, does not cost any more—theoretically—than between 50 and 200.

In reality there is no utility in pushing compression further, because the damaging influence of the conjugate volume (p. 112) becomes in this case very apparent, and causes itself to be felt from two different points of view.

On the one side,  $\frac{a}{v_1} - \frac{a}{v_0}$  is far less increased than might be supposed, increasing at 0° C. only from 2400 to 3800 kgms., being a gain of only 1400 kilogrammeters against over 3000 which might have been hoped for.

On the other hand,  $p_1 v_1$  is considerably increased by comparison with what it was at 200, which is a very unfavourable fact. At 0° C.  $p_1 v_1$  under 500 atmospheres is greater than  $p_0 v_0$  at 125 atmospheres by 3600 kgms., and is greater by 1000 kgms. still at -50° C. instead of being less by 400 kgms., as was the case from 50 to 200 atmospheres. This difference of 1400 kgms. completely sets off all the gain due to the increase of internal work.

As to the co-efficient of expansion fixed by Linde at—

$$\frac{200}{50} = 4$$

we can manifestly have no interest in reducing it save exactly at the moment when the hatched area (Fig. 47) more than offsets the gain realised over the work of compression, and in this respect also, we find that there is no advantage in departing from the conditions laid down by Linde.

We will proceed no further, and shall not ask for more exact information of a process whose essential object, let us repeat, was to establish the main features of the mechanism of expansion with internal work, and to throw light on the work, which has aroused for the learned professor of Munich the admiration of all physicists. Perhaps it might have been interesting to arrive closer at the meaning of things by introducing into the question of internal pressure, following the example of Clausius and Sarrau, a factor diminishing with the temperature, or by making this internal pressure vary in accordance with the ideas of Amagat. We have not thought it necessary, however, seeing, on the one hand, that the lowest temperature, which we have had occasion to consider, from the point of view of yield is, as we know the initial temperature of admission, never lower than  $-50^{\circ}\text{C}$ ., and that, on the other, the pressures employed are still far removed from the values capable of introducing important anomalies in the law of variation of internal pressure formulated by Van der Waals. It is otherwise interesting to find that the conclusions, such as they are, of this theory are in perfect harmony with the teaching and the results furnished by practice.

## CHAPTER VII

### EXPANSION WITH EXTERNAL WORK THAT CAN BE RECUPERATED.

WE have just estimated at 90 calories per h.p. hour the theoretical production of cold brought about by expansion by simple outflow.

There is nothing there which is beyond the means of expansion with external work, and this chapter is dedicated to the proof of this statement.

Ever since 1898 Lord Rayleigh estimated\* that if Linde's expansion were effected against the vanes of a turbine, however inefficient the turbine might be, you could not fail, by bringing this external work into play, to very largely improve the results. But we have seen that it was not through misunderstanding its valuable qualities that expansion with exterior work has been so long put on one side, but because of the practical difficulties encountered in its realisation.

Before indicating by what means the author had been able to succeed in solving these, it will be well to recall at first starting the initial principle of expansion with external work by commenting in a few words upon the diagram (Fig. 49).

The expansion machine, which is nothing more than a simple compressed-air motor, is connected with the compressed air pipes through the central compartment A of the exchanger M.

\* 'Nature,' lviii, p. 199, 1898.

After having worked in the machine, and having been cooled through the fact of its work, the expanded air is expelled into the atmosphere through the peripheral compartment *b* of the exchanger. By the sequence of effects which we know well, and on the supposition that we are not stopped on the way neither by congelation, nor by seizing, nor by penetration of external heat, the temperature is progressively lowered until at a given moment it

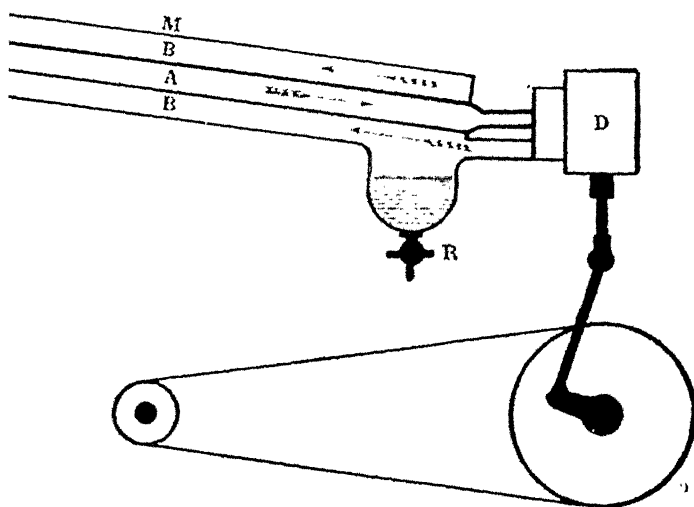


FIG. 49.—Diagram of expansion with external work.

attains the temperature of liquefaction for air. From this moment onward the liquid air thus furnished accumulates in *R*, whence it can be periodically abstracted from the outside.

The production of cold depends in this way in principle upon the abstraction from the air itself which is expanded the energy which we can abstract in the form of external work, or, in other words, upon the adiabatic expansion of air in the expansion cylinder. Accessorily, be it understood, we equally profit by the internal work which at a



pressure of 40 atmospheres is responsible to the extent of some 5 per-cent. for the cold produced.

It will be seen, nevertheless, that if we operated in this way—that is, followed the ideas of all the experimenters who have preceded Claude—the results of the procedure would be unmitigatedly deplorable; but by successive stages, which the author will explain, he has shown that it is possible to extend the yield beyond that of the isothermic expansion at the critical temperature of air ( $-140^{\circ}$ ) and even of oxygen ( $-118^{\circ}$ ).

Omitting the first case, we shall establish that under these conditions the theoretical limiting yield of expansion with external work, including internal work, is not less than 170 calories per h.p. hour.

#### **AUTO-LUBRICATION: PETROL-ETHER.**

Claude's point of departure having been amply justified by these results it remains to describe the somewhat wearisome and long stages by which Claude had to pass since 1899 to achieve the practical processes which, alone with Linde's, are actually used on an already considerable scale for the commercial production of oxygen.

Before proceeding further, nevertheless, it will be necessary to point out that Claude would have certainly had some hesitation in taking up a field already so well worked, on his own. To decide him to do this, nothing short of the encouragement and precious advice, always at his disposal, which the illustrious successor of Claude Bernard, d'Arsonval, and the great scientist Potier, whose name will always be recalled with grateful affection by that numerous band who were his debtors, could have sufficed. What such support meant for Claude in the heavy task he was undertaking, what comfort it brought him in the hours of discouragement, none too few during the six long years

of struggle before success came, is part of his gratitude to avow here.

Care must be taken also not to forget the valuable aid which Claude received through the confidence which the members of the *Société de l'Air Liquide* (Liquid Air Co.), and especially their chairman, Paul Delorme, always reposed in him.

Of certain difficulties pointed out previously (p. 79) as offering obstacles to the application of expansion with external work, Claude was able from the first to convince himself that the only factor which really counted was the freezing of the lubricants. We have, it is true, pointed out, on the other hand, the difficulty of protecting the expansion machine against the re-entry of external heat, but if the problem is difficult, it is not insoluble; and we would add that, even if it were so, the process would not lose much therefrom, because, save in very small apparatus, the smallness of the expansion machine in comparison with the whole apparatus would prevent this fact from becoming really important. Claude, on more than one occasion, has happened to work his machines stripped, under the sole protection of the layer of rime which the atmosphere provided gratis, and he found it very difficult to determine any falling off in the frigorific yield.

As far as the water and the carbonic acid in the air are concerned, whose freezing has also been alluded to as against the process, it is very certain that it is best to get rid of them by careful purification. Expansion with external work in this respect does not fly a different flag to its predecessors.

In point of fact, we repeat, the only thing that counts are the difficulties of oiling.

This is equally the conclusion to which the English engineer Thrupp, arrived, and in an interesting patent\*

\* English patent No. 26,767 of 1898.

he has pointed out an ingenious means of solving the difficulty, a means consisting of employing for expansion a turbine possessing a shaft of sufficient length to remove the bearings of this shaft from the action of low temperatures. Claude adopted on his side other means, and instead of turning the difficulty he preferred to deliver a frontal attack. The starting-point of his reflections, was furnished by an observation made during the course of an experiment. Liquid air, in a similar way to water, *wets* metals which are in the first place cooled down to its temperature.

Let us suppose, thereafter, that by an indeterminate device we should succeed in bringing the motor machine in which we wished to work the expansion down to the very low temperature to which this expansion brings the liquefaction. Starting from this instant, as the liquid air flows abundantly in the machine, this would find itself in the same conditions as a hydraulic turbine. We know that in these apparatus the lubrication of the frictional parts is assured, apart from any external means, by the water itself which bathes them. It appeared to Claude that it should be the same in his expansion machine if he succeeded in bringing it under the conditions of temperature in question, as its working could thereafter be prolonged indefinitely, irrespective of any external agency, by the *auto-lubrication* carried out by the liquid air.

Thus this difficulty of greasing, which had been held till then to be an insurmountable barrier by all preceding experimenters, turned out to be in reality evanescent; it is limited to the starting of the apparatus, to the period comprised between the start of the operation and the moment at which, through the combined effect of expansion and the exchanger of temperatures, the point of liquefaction for air is attained.

Now let us suppose that we cool the apparatus without working the machine. We could use for the purpose

either expansion by simple outflow, or even liquid air borrowed from another source, and which we could pour into the machine, until it became cold together with a portion of the apparatus.\* Then, according to what has preceded, it will suffice for us to put it in motion to ensure the continued production of the liquid air. Thus already the problem appears to be less insoluble than we at first thought.

Truly the artifice is not one to be specially recommended. To ask expansion with internal work under considerable pressures to make good the means to get Claude's own apparatus out of the ditch, would have been somewhat humiliating for a new process, and of all the greater difficulty in that at the time of his first attempts he could have hardly obtained the considerable volumes of liquid air required for the experimental proof of his ideas. It was necessary, therefore, for him to endeavour to make his machine able to suffice unto itself, able to succeed by itself independently of all auxiliary frigorific help, at the temperature of auto-lubrication.

Claude thereupon remembered that in the course of experiments made in connection with quite another matter† some months previously he had had occasion to appreciate the remarkable incongelable qualities of the volatile hydrocarbons of the petroleum family. When all others of the common liquids were instantly congealed in liquid air, these hydrocarbons, which are no other than the ethers of petroleum or other volatile essences used in connection with motors, support without change the effect of these temperatures.‡ At the most they change their usual perfect fluidity

\* French patent No. 324,715.

† 'Proceedings of the Academy of Sciences,' August 21st, 1899: "On the Magnetic Properties of Iron at Low Temperatures."

‡ This remarkable property of petroleum ether had been indicated without Claude's knowledge, in 1896 by Kohlrausch, who applied it to the manufacture of special thermometers for low temperatures.

under these conditions for a syrupy consistency absolutely comparable with that of commercial lubricants, which are, moreover, nothing else but superior homologues of the liquids in question. This approximation itself was very instructive. It permitted of the hope, that when introduced in the expansion machine, these petroleum ethers, which at ordinary temperatures are *the exact opposite* of lubricants, would of themselves acquire through the fact of cooling the qualities required by a lubricant.

On the supposition that this hope was justified the problem of greasing was solved. Being safeguarded on starting the machine by ordinary lubricants, and safeguarded at very low temperatures by petroleum ether alone, lubrication could manifestly be kept perfect at all the stages of cooling by the successive use of mixtures of ordinary lubricants with an increasing proportion of petroleum ether.\*

**First attempts.** — Claude was not long in verifying the exactitude of these forecasts. An experimental apparatus was constructed at the end of 1899 with the able co-operation of Vettiner, works manager of the Saint-Maudé Tramways—a rather singular apparatus composed of a small vertical motor worked by compressed air from the Salmson Works, with a piece of wood for a brake, connected with an exchanger of temperatures composed much to everyone's surprise of a zinc gutter pipe five centimetres in diameter and some ten metres in length, containing some dozen copper tubes intended to conduct the compressed air.

The pressure in this was only 12 atmospheres. Ordinary lubrication under pressure allowed of the introduction in the cylinder, according to the progress of cooling, of an ordinary lubricating oil to which an increasing proportion of petroleum ether was added.

\* German patent 165,744, February, 1900.

After some preliminary trials a decisive experiment was attempted.

It was at the end of 1899, on a cold snowy night of November, within the somewhat forbidding tramway dépôt of the Bastille-Charenton Tramways, a totality of conditions of very doubtful comfort, with which Claude's circumstances and his occupations for the time being, compelled him to be satisfied.

The experiment was commenced, and it was not long before he had the satisfaction of finding that everything was behaving better than expectation. From the moment of starting, moreover, the rapid fall of the toluene thermometer placed in the air exhaust of the machine was apparent, whose graduation had been conscientiously extended by the maker down to  $-150^{\circ}\text{C}$ .

• Three hours after the start, the lowest point of this graduation had been attained and the thermometer was still falling! A few minutes later the liquid in the thermometer had entirely frozen! A few more minutes and the machine had given over without having furnished any liquid air. The pity of it, but, in point of fact, not even so much had been asked of it on this occasion, and Claude sought, enchanted, the tramway car which was to serve him as sleeping quarters for that night. Who would have dared to tell him at that moment that two years and a half of effort still lay between him and his first drop of liquid air?

Now, one day, several years later, Claude found out by an extraordinary chance what had caused him to fail in his first experiment, and this, his enthusiasm helping, thus enabled him to obtain, with the assistance of a few friends, the necessary funds to undertake without further delay some more serious experiments. He thereupon carried out some experiments with toluene at low temperatures, and at a given moment had to determine its temperature of solidifi-

cation. Fancy his astonishment at seeing it solidify into a mass at about  $-100^{\circ}\text{C}.$ ! What, then, of the  $-150^{\circ}\text{C}.$  of his previous experiment, and his fine enthusiasm? Thus when Claude had exulted at seeing the liquid congeal at  $-150^{\circ}\text{C}.$ , at most it had touched  $-100^{\circ}\text{C}.$ , and this was, moreover, the limit of his efforts since his machine gave over an instant after.

Now, try to appreciate his bad luck. It suffices to recollect that  $-100^{\circ}\text{C}.$  is insufficient, joking apart, to arouse any enthusiasm; it is too indecisive to get on with, since Solvay, before Claude, had obtained  $-92^{\circ}\text{C}.$ , and Claude would have probably remained nonplussed had it not been for the very gross error of a well-known instrument maker. It has been stated above (p. 95) how useful Claude had previously found his ignorance of a special point in the theory of gases, all of which would almost prove that with ignorance and imperfect tools everything can be achieved!

On September 10th, 1900, Claude was able to announce to the Academy of Sciences the first results of his new apparatus installed at La Villette, at the compressed air works of the omnibus company. The existence of these works, which at the time were almost unique of their kind, proved an exceptionally favourable circumstance for Claude, be it noted, and he has never ceased testifying to his gratitude to the engineer in chief, Monmerqué, for the inestimable favour he conferred in throwing the works open to him.

In this note of September 10th, Claude stated that his anticipations had then already been to a large extent confirmed. The admission pressure of the air to the machine was only 25 atmospheres. Now, notwithstanding the extreme relative insignificance of the pressure, and notwithstanding the use of appliances whose total weight exceeded 800 kgrm., worked by a machine whose

expansion cylinder was of only 1 litre capacity, the expansion proved to be very effective; thanks to the successive employment of three or four suitably graduated mixtures of petroleum ether and valvoline, the temperature at the exhaust fell in an hour and a half to  $-140^{\circ}\text{C}.$ , this time properly measured with the aid of an electric thermometer constituted by a constantine iron couple connected with a galvanometer.

From this moment it was possible to do away with all lubrication. The temperature progressively fell to  $-170^{\circ}\text{C}.$  without the working of the machine ceasing to be excellent during a period of time which on several occasions was from five to six consecutive hours. It appeared, therefore, that the idea of auto-lubrication had been completely confirmed, as liquid air was certainly formed as sediment at the end of each expansion, and this sediment sufficed to ensure the lubrication.

In this first note Claude pointed out in addition that expansion with external work had appeared to him to be so efficient that he had been able to obtain temperatures of the same order as those mentioned, that is,  $-160^{\circ}\text{C}.$ , with pressures of only 7 atmospheres.

**First successes.**—In all these first trials, however, in spite of repeated attempts relating to the arrangements of the exchangers, their dimensions, to the desiccation of the air, and of its supplementary cooling, not one drop of liquid air had been obtained, and none came till about the middle of 1902.

Claude had commenced to despair of ever being able to cross the narrow interval which separated him from his goal, when he had the idea that the very low temperature of exhaust regularly obtained with each of his trials, although insufficient to bring about the liquefaction of the air under the feeble exhaust pressure, could certainly bring about the liquefaction of a portion of the air if still subjected



to the pressure of admission. A simple piece of reasoning certainly, and which there was very little excuse for having reached at such a late date, were it not that besides the scanty time which Claude's other occupations permitted him to dedicate to the investigation, the horizon was terribly foggy on every side round this novel field which he was working with very restricted facilities, and where each trial raised some new problem.

It was on May 26th, 1902, that Claude reflected as above, and it was a Sunday. Now, that same day, it will be seen that Claude had his reasons not to waste time; he had a tube of small diameter terminated by a cock and fed with air under pressure taken from the cold end of the feed pipe of the apparatus, fitted in the exhaust pipe. As soon as this was done the machine was started, and two hours later Claude had the satisfaction to at last see a thin thread of liquid escaping from the cock, and filling little by little one of the three litre liquid air holders which had so long waited for its appearance.

It is not necessary to insist upon Claude's profound satisfaction, which was not alone on account of the scientific result so long hoped for, but, in fact, was more than doubled in his case by circumstances of quite another order. A shareholders' meeting had to be called on the following day whose patience was exhausted and to whom proposals had to be made for completing the experiments.

This first improvement, perfected little by little by progressing methodically along the alluring path, finally resulted in endowing the apparatus with a capacity of output, of 25 litres of liquid air per hour. On June 30th, 1902, d'Arsonval notified the Academy of Sciences of the definite success of Claude's efforts, omitting, however, for reasons of commercial protection, the mention of the device which had made them succeed.\*

\* 'Proceedings of the Academy of Sciences,' June 30th, 1902.

A few days later a committee of the Academy came to La Villette to investigate by inspection the working of Claude's apparatus. Thenceforward the reason was known.

**Faults of expansion with spontaneous liquefaction.**—Some reasons have already been given for the considerable time expended in obtaining this first success. Probably other extenuating circumstances might be alleged in excuse.

Theoretically, nothing stands in the way of the spontaneous liquefaction of the air at the limit of expansion: it is sufficient that in the frigorific balance-sheet expansion should more than compensate for the total losses due to friction in the expansion cylinder, to the inevitable penetration of the external heat, and to the no less fatal imperfections of the exchangers of temperature, which in Claude's first attempts allowed the air to escape  $15^{\circ}\text{C}$ . colder than it had entered.

The non-production of liquid air appeared to be, therefore, more than anything else an indication of the considerably exaggerated importance of these unfavourable circumstances and Claude turned his efforts before anything to counteracting their influence.

This reasoning was not illogical, for without ever attaining to extraordinary yields, Claude succeeded in making liquid air by spontaneous liquefaction of the air at the limit of expansion, although more extended experience enabled him to devise more efficient and better insulated exchangers. But immeasurably more was yet to be gained by improving, as we shall see, the efficiency of expansion itself. It was to this ideal that Claude dedicated his attention, in consequence of the scanty success of his efforts in the other direction, and it is to this that the improvements of which we have spoken above, directly led.

We are thus brought, after having praised the process, to insist very much upon its very grave defects. In the first place, we have admitted that liquid air is a lubricant.

Now, in reality, if it is effectively such, it is nevertheless a mediocre one at that. Some very careful experiments carried out in the laboratory of the Conservatoire of the Arts and Crafts, with the invaluable help of Péro, the manager of this establishment, left no doubt in Claude's mind on this point. And the appearance of liquid air in the machine, in addition to the "water-hammer action" of a rather original fluid, was accompanied by a notable increase of friction, and therefore by a corresponding destruction of the liquid air produced.

If, therefore, it be easy to stop all lubrication as soon as liquid air is produced, it does not follow that it is in certain respects to be recommended to do so. But beside this consideration of a practical kind, a far more important point is the following:

We have stated above that if to exhaust the whole effect of expansion we should expand down to atmospheric pressure, a certain portion of this air would thereupon liquefy at the end of each stroke of the piston.

Under these conditions it is very evident that the final temperature of the expansion is  $-190^{\circ}\text{C.}$ , since this is the temperature at which liquid air can exist under atmospheric pressure. The non-liquefied portion of this air—that is, over nine tenths thereof—quitting the machine at this very low temperature to enter the exchanger (see Fig. 49), will consequently cool the compressed air very energetically. Even were air a perfect gas, the work of expansion would have to suffer from this state of affairs, for, with such a gas, the work of expansion necessarily diminishes with the temperature, to become nothing at absolute zero. But with air it is far worse than this, because it reaches the machine without doubt not even at  $-175^{\circ}\text{C.}$  or  $-180^{\circ}\text{C.}$ ; moreover, we know the phenomenon of progressive increase of specific heat limits the fall of temperature (p. 141) at  $-135^{\circ}\text{C.}$  or  $-140^{\circ}\text{C.}$ , that

is, in the immediate vicinity of its liquefaction temperature under 40 atmospheres' pressure. \*

Now we know what a profound perturbation is produced in the elastic properties of gases by its proximity to liquefaction; far more contracted than is allowable under the laws of Mariotte and Gay Lussac, the compressed air which enters the machine is not yet a liquid, but it is almost no longer a gas; its expansive properties are, so to speak, done away with, and the external work of expansion becomes detestable.

Furthermore, we can give more exact details.

Let us consider the conditions at the temperature of  $-135^{\circ}\text{C}$ . By referring to Witkowski's table (p. 129) and comparing the horizontal line relating to 40 atmospheres with the last line relating to a perfect gas, we shall see that the air under 40 atmospheres' pressure occupies at this temperature of  $-135^{\circ}\text{C}$ . *half* the volume of a perfect gas. In comparison with the formulæ of thermo-dynamics relating to perfect gases, we have, therefore, to introduce into the machine at each stroke of the cylinder 100 per cent. excess of air, and this, to enable us to obtain in this stroke *far less* work, the pressure during expansion falling more rapidly than with a perfect gas, because of the great fall in temperature due to the simultaneous action of the diminution in specific heat and the mechanical effect itself of expansion. Without investigating for the moment the exact value of this work, it is, nevertheless, very certain, in consequence of the preceding remarks, that this work for an equal quantity of air only reaches *one third* of that which a perfect gas could yield starting from the same temperature. And we can well understand how much the circumstances would be aggravated if the temperature of admission were lowered to  $-140^{\circ}\text{C}$ ., temperature at which the volume of the compressed air falling to *one quarter* of that of a perfect gas, it would be

necessary to admit at each stroke 300 per cent. excess of air to obtain in this case hardly any work at all!

These forecasts are completely confirmed in practice. When an expansion machine reaches these conditions of extreme temperature, the consumption of air increases in an enormous ratio out of all proportion with that which would correspond with the theoretical Gay Lussac effect of the fall in temperature, while the efficiency of recovery diminishes very considerably.

We see that it was no exaggeration to qualify this influence of the imperfection of the gaseous state as disastrous, and qualified by such a serious defect expansion with external work cannot yield as it stands satisfactory results. This was the cause of Claude's defeats during the three long years of which we have spoken above.

#### LIQUEFACTION UNDER PRESSURE.

Claude was lucky enough to find a sovereign remedy for this situation, whose use is indispensable to place expansion with external work in a position to keep the promises made on its behalf by theory.

It is in an increase of temperature that the remedy in question is to be found.

It would suffice, moreover, to raise the initial temperature of expansion relatively very little to get clear of this zone of profound perturbation, which is localised, for each pressure, in the immediate vicinity of the corresponding temperature of liquefaction. An example was given just now which furnishes a measure of the improvement which might follow upon a slight rise of temperature, when we said that at  $-135^{\circ}\text{C}$ . the anomalous contraction amounts to only 100 per cent., when it amounted to 300 per cent. when it was only  $5^{\circ}\text{C}$ . lower.

And if, for example, with our working pressure of 40 atmospheres, we could raise the initial temperature from

135° C. to 100° C., we should reduce the excess of expenditure, the waste of compressed air from 100 per cent. to under 20 per cent., and at the same time increase in an enormous ratio the work of each stroke of the piston.

But it is not a question here of only obtaining much cold during expansion; it is also the question of obtaining this cold under such conditions as to imply liquefaction. And in this respect it seems to be a paradox to seek to raise the temperature when in the case of liquid air the

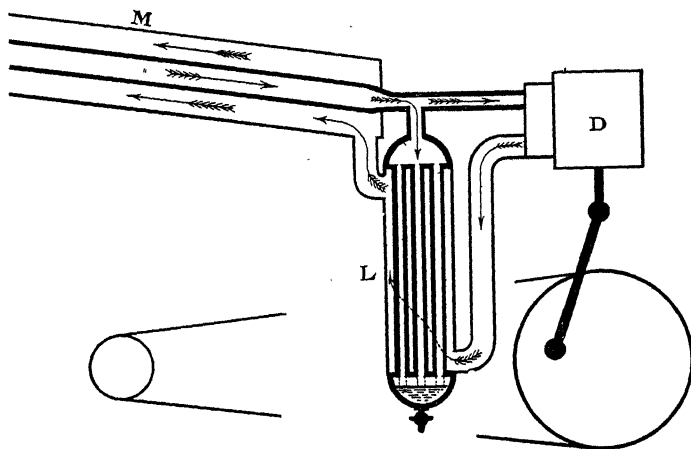


FIG. 50.—Liquefaction under pressure.

whole secret of success seems absolutely dependent on obtaining extreme refrigeration.

This is how the author has solved the problem.\*

The air which has just been worked through the machine, instead of being partially liquefied as previously, is made (Fig. 50) to circulate from below upwards around the tubes of what we might call a *liquefier*, that is, of a bundle of tubes supplied with a portion of the cold compressed air of the feed circulation of the machine.

It will be noticed that this is a repetition on a larger scale of what Claude had realised in his first experiments

\* German patent 192,544.

at La Villette by means of a pipe of compressed air placed in the exhaust.

This compressed air, under the combined effect of the compression to 40 atmospheres and the extreme cold of the expanded air circulating around it, will thereupon liquefy; but as it is a general law of physics that the temperature of a gas is raised proportionately to the pressure to which it is subjected (p. 12), it will be liquefied no longer at  $-190^{\circ}\text{C}.$ , but at  $-140^{\circ}\text{C}.$ , which is the critical temperature of the air. On its side the expanded air, which must abstract heat from the compressed air to liquefy it, is heated up by this circumstance to  $-140^{\circ}\text{C}.$ , and even  $-130^{\circ}\text{C}.$ , because through its methodical circulation from bottom to top of the liquefier, it has not only to liquefy the air in the liquefier, but has first to cool it, in spite of its very high specific heat from the temperature of admission down to  $-140^{\circ}\text{C}.$

The expanded air passes, therefore, from the liquefier into the exchanger no longer at  $-190^{\circ}\text{C}.$ , as previously, but at about  $-130^{\circ}\text{C}.$  only, and cools the compressed air very much less as a consequence. The latter only reaches the machine, on an average, at  $-100^{\circ}\text{C}.$ , and you can easily imagine, after what has been said, the *enormous advantage* that a similar increase of temperature can produce in the conditions of expansion.

To ensure that the raising of temperature in question is effected, it is naturally necessary to withdraw the liquid air produced in the liquefier as it is produced, and the extraction valve must be worked with this object in accordance with the indications of an electric thermometer fixed at the admission to the machine, so as to maintain a temperature of admission close to  $-100^{\circ}\text{C}.$  If closed too much, the extraction valve allows the liquid air to accumulate in the liquefier, the exhaust air is no longer heated up sufficiently, and the temperature of admission is

lowered. If open too much, the valve allows non-liquefied air to escape as sheer loss and the yield is lowered.\*

The extraction is unavoidably accompanied by an abundant evaporation corresponding with the fall of pressure. Before being added to the exhaust air, these very cold vapours are employed to cool down the liquid air to be extracted as close as possible to  $-190^{\circ}\text{C.}$ , and to reduce in this way to a minimum the harmful evaporation to which they themselves are due.

The object of this device has been questioned, particularly in Germany.† It is, however, very easy to establish its efficiency unquestionably. It is sufficient to do away with the extraction from the liquefier for a time: the bundle of tubes gets filled up with liquid air, and from this moment on, the part played by the liquefier is done away with; the yield of air, indicated by a pressure gauge which measures the counter-pressure balanced by the passage of the expanded air in the exchanger, far from being diminished, *rapidly increases* after a few seconds. Besides this, if the machine is working a generator, the product of the voltmeter and ampèremeter readings falls with a surprising rapidity notwithstanding an increased yield which may even be doubled. We obtain in other words comparably less energy from the air treated under these conditions, and the output of liquid air is nothing less than *plorable*. Finally, the machine itself acquires under these conditions a profound change in behaviour: it appears to be suffering, it *clatters louder* if its parts have the slightest wear; this is due to the presence of liquid air in its interior; furthermore, if the stuffing-boxes of the piston or of the working gears are not perfectly tight, the

\* It should, however, be observed that expansion with internal work is in this very efficient, and a great deal is liquefied, because in point of fact this outflow substitutes an expansion with internal work and auxiliary cooling of an extremely rare character.

† 'Zeitschrift für die gesamte Kälteindustrie,' December, 1907.



tendency to escapes is far more pronounced, and there are no longer simple jets of "vapour," but great opaque clouds which escape and complete the inefficiency of the frigorific yield.\* Working is so unsatisfactory under these conditions that we have even observed under these circumstances that the *cylinders have cracked*.

Then, if the outlet cock is opened again, the liquefier is emptied, the temperature rises, the yield of air diminishes, the machine starts again gaily and the power recovered increases visibly.

Moreover, whilst it has been impossible ever to exceed with spontaneous liquefaction an output of 0.2 litres of liquid air per horse power hour, this is increased by the very simple artifice of liquefaction under pressure to 0.71 litres.†

This figure applies to machines dealing with compressed air furnished by a power of 75 H.P.

The efficiency of the device cannot give rise to the slightest doubt either on the ground of experience or of the data quoted above; but we shall be able to confirm it further on. It is therefore not at all doubtful that this constitutes an accessory which is henceforward indispensable to expansion with external work, whatever the expansion device may be, either a piston machine or a turbine; however slight, on the other hand, the pressures which have to be used may be; and, moreover, there is always an advantage in not liquefying spontaneously, but in delivering the exhaust round an arrangement of pipes, fed with air at its pressure of admission, however feeble that may be; for by working in other ways, inferior pressures entail lower pressures of admission because of the lower specific heat when cooled, of air compressed to a lower degree; it results therefrom that besides the closer vicinity

\* It should not be, moreover, forgotten that the escapes at low temperatures are horribly prejudicial to the output; the gaseous air which escapes at  $-190^{\circ}$  C. is equivalent to the loss of half its weight in liquid air.

† 'Proceedings of the Academy of Sciences,' June 11th, 1906.

and consequent increased mischievousness of absolute zero, there exists always the important anomaly of contraction.

The better course in this respect would be even to face the complication of a distinct feed for the liquefier with air at its critical pressure.

It was to some extent the desire to avoid this complication and to maintain a single circulation of compressed air, while benefiting from the advantages of the critical pressure, which fixed at 40 atmospheres, Claude's choice of normal pressure for his *liquid air* machines.\*

Naturally with this device the liquid air is no longer produced in the machine, and we can no longer count on that to ensure lubrication. It is therefore necessary in this case to lubricate wholly with petroleum ether, but this, even, is a further advantage, because, as was stated previously, liquid air is but a poor lubricant.

It has further been remarked that the fall in temperature on starting being very rapid, it is useless in practice to use the succession of less and less congealable mixtures which Claude used in his first experiments. From the commencement, lubrication can be effected with petroleum ether of 0.675 to 0.700 density, the common petrol of the motor car. The result is slightly less satisfactory at first, but the transitory stage is quickly passed, and in this way the danger of seeing certain vital organs of the machine frozen through the tardy substitution of a less congealable mixture is avoided.

Claude has quite recently succeeded (1912) in doing away with all lubrication, even during the period of starting working, and to reply in this complete way to the reproach which had been frequently addressed to him on this point, thanks to a strange property which leather possesses, and which he discovered. Constituting a fact which is an excep-

For the *oxygen* machines, where the question, as we shall see, is only to compensate by the expansion for the loss of cold in the system, the ruling pressure is fixed to the amount which permits of this exact compensation. (Chap. XIX).

tion to the almost universal rule, according to which organic solid bodies become hard and brittle at low temperatures, leather, after being suitably treated, preserves, on the contrary almost all its qualities of suppleness as well as mechanical resistance. Claude has therefore been able to substitute for the metallic rings of the pistons of his expanders stamped leathers, which have the triple advantage of not requiring, as has been stated, the least lubrication, of not giving way as often as the metallic rings did, and of doing away with all wearing in the cylinders, whose sides were rapidly worn away in the apparatus in the form of a black and combustible powder.

In Claude's first attempts he used exclusively draw-valve machines. Fig. 51 shows the machine of this type which gave him his first results.

Subsequently, but not without hope of reverting thereto, these draw-valves were given up because of various practical drawbacks, and preference was given to trap-valve distribution. Fig. 52 shows this type, worked out by Claude's assistant, Le Rouge, and embodied in the present simple expansion machines with liquefaction under pressure of the Liquid Air Company. It is needless to say that many a trial and error has been necessary to determine this type of machine, working as these do at temperatures where the properties of the various metals composing them are completely changed.

More particularly the ordinary metals, if they actually have their resistance to rupture increased in a large measure, have their fragility largely aggravated, and break like glass under a blow which is only slightly violent; it has often occurred that expansion cylinders made of very thick steel have been broken in pieces, and especially when the machine was working at too low a temperature (p. 172).

This happily produced no dangerous consequences for the workmen, because the burst necessarily occurred at

the end of the stroke, at the moment when the cylinder was more or less empty of air.

It is useless to add that these accidents have been rendered very rare by a deeper study of the details of construction, and now, curious to state, while the makers have

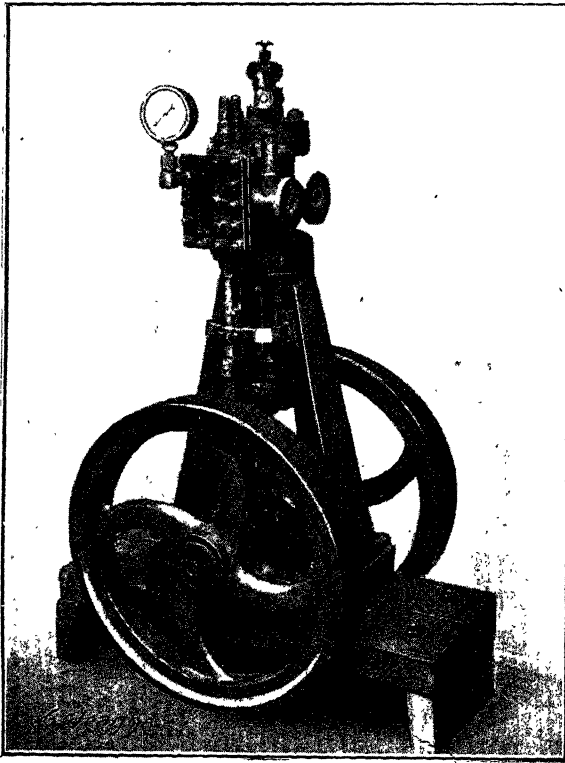


FIG. 51.—The first piston machine which furnished liquid air.

oubles which are relatively frequent, with the ever well known but still somewhat barbarous and brutal appliances which air-compressors are, they have, so to speak, none at all with the newborn appliances, the expansion machines for liquid air.

We would mention in passing, in connection with these

troubles due to compressors that, most interesting perspectives for the future of the liquid air industry have been disclosed by the recent application in the U.S.A. (1909) of the principle of water-suction tubes for obtaining compressed air directly, from waterfalls or even from tides.

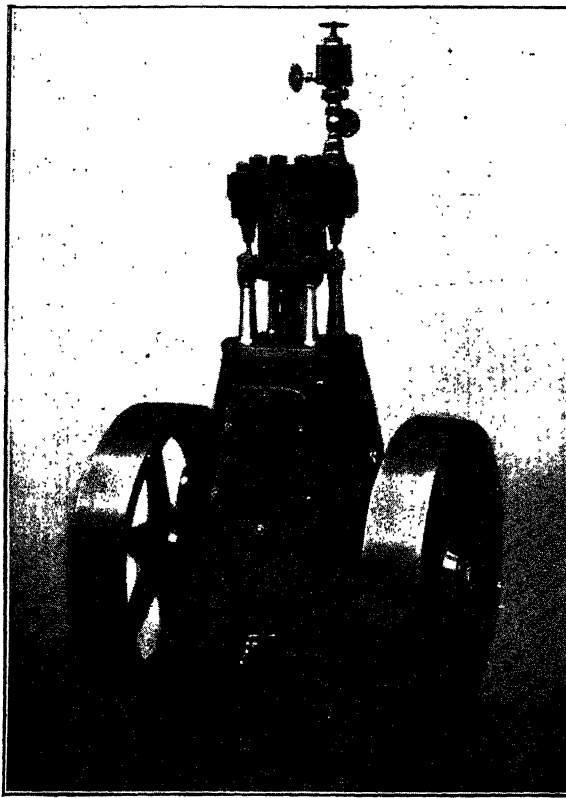


FIG. 52.—The actual type of machine with simple expansion of the "Liquid Air Company."

**Some reflections on the recuperation of energy.**—The results indicated above, on the credit side of liquefaction under pressure, have been achieved by taking advantage of the energy *recuperated* during expansion.

It should, furthermore, be remarked that recuperation is

one of the most interesting characteristics of expansion with external work: this method of expansion is more efficient than the other, not only because we obtain more energy from the gas, but also because this energy is obtained (excepting the internal work) under the form of mechanical work, through the effect itself of the device of expansion; this recuperated mechanical work may be utilised in diminution of the work of compressing the air, so that the advantage of extracting from the compressed air the maximum of work, by means of the type of liquefaction under pressure, and of other types which we shall indicate presently, acts in a certain way as if it were raised to the square, since both the cold produced and the energy recuperated are increased at one and the same time.

The question might be asked if it would not be possible to go still further along the same road, and to recuperate during expansion all the energy expanded during compression, since expansion, in simplest terms, is the inverse phenomenon to compression, in which case it would be possible to obtain liquid air with an expenditure of *no energy at all*.

The supporters of this way of arguing would not fail to point out that this consequence is not absurd from the point of view of the conservation of energy, since there is no question here of *creating* energy. The liquid air obtained is only, in point of fact, ordinary air *less* some heat, and the heat thus rendered available can be done something with—say, can perform work. It is, therefore, a concession on their part to simply admit that the liquid air obtained may not cost any energy. They might quite as well contend that not only does it cost none, but that it enables the production of some. Such an admission, moreover, would be an easy one for them, because since the liquid air can, when finally evaporated, furnish an appreciable amount of mobile power, we should possess in any case an indirect means of

transforming the heat of the environment into mechanical work.

Be it understood that such an idea is perfectly chimerical. Even if we leave the imperfect capacity of compressing and expanding machines out of account, the energy developed by expansion is necessarily much weaker than that absorbed through compression, as it is carried out at an absolute temperature twice as low in the one case as in the other, and Carnot's principle—which has faced many another attack—can still afford to consider these fallacious attempts to get round it, with unruffled calm.

It seems necessary to insist somewhat on this matter, because it is difficult to estimate the number of investigators who are haunted by this more or less avowed idea that liquid air, being ordinary air *less* some energy, we should be able to recuperate on the one side this energy under the form of mechanical work, and on the other the liquid air, and in this way supply without expense these two great manufacturing necessities, motive power and cold. This seems to be in the matter of perpetual motion the last boat to leave the shore, a boat in which, we must acknowledge, many passengers have embarked.

But if this way of looking at things is certainly chimerical, the influence of recuperation on expansion with external work is, however, incontestable. The saving resulting therefrom, from the point of view of expenditure of energy, can attain 25 per cent. in well-conditioned machines, and it is one of the elements which secure for this method a distinct superiority over expansion by simple outflow.

**Improvement of the terminal stages of expansion; compound expansion.**—Encouraged by the excellent results given by liquefaction under pressure, Claude was led to take one step forward.

It is clearly manifest, that the foregoing solution was

incomplete. Though by its means, through the air reaching the machine in less cold condition, the first part of its expansion is certainly effected under good conditions, the rapid cooling produced by the expansion, both by its direct effects and by the fall in specific heat with the pressure (p. 146), will have soon brought about the reduction of the air to conditions approximating those of absolute zero and the imperfections of the gaseous state will have reasserted

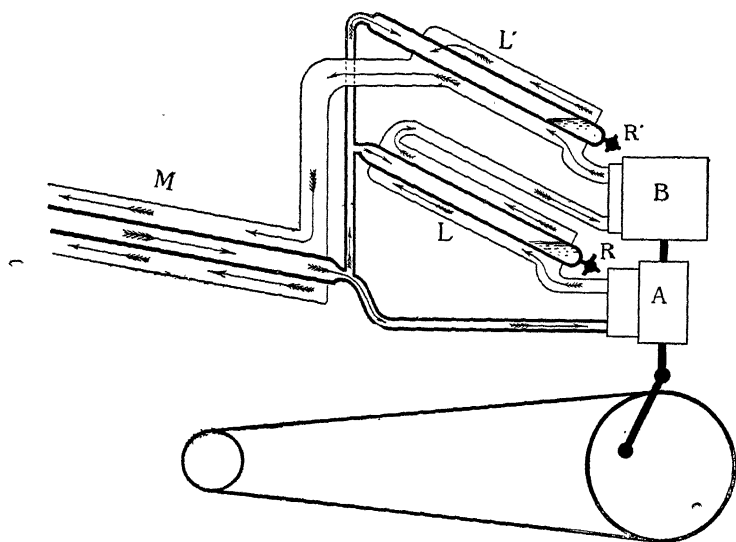


FIG. 53.—Compound liquefaction.

themselves, so that the whole terminal stages of expansion are once more accomplished under bad conditions.

Claude designed a first means of remedying this defect.\* This consisted in stopping the expansion at a point yielding a temperature clearly inferior to the critical temperature, such as, for example,  $-160^{\circ}\text{C}$ . The air thus *partially expanded* is passed into a first liquefier *L* (Fig. 53) as shown from below, so as to bring about the liquefaction of a portion of the cold compressed air in the feed circuit, which is subjected in ordinary types of Claude

\* German patent 192,594.



apparatus to a pressure close to the critical pressure. This heats the partly expanded air up to  $-140^{\circ}\text{C.}$  or  $-130^{\circ}\text{C.}$ , and enables it to go and complete its expansion under much better conditions in a second cylinder, whence it will proceed to a second liquefier  $L_1$  to bring about a second

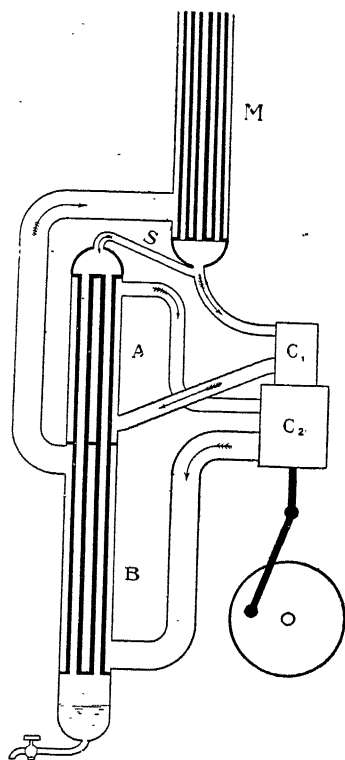


FIG. 54.—Machine with compound liquefier.

liquefaction analogous to the first, to be thence transmitted to the exchanger.

In practice (Fig. 54) the two liquefiers are united in a single bundle of tubes fed by a single branch “S” of cold air under pressure. The air from the second expansion, which is generally colder, circulates similarly from bottom

about not only the completion of liquefaction, but also the cooling below the critical temperature of the liquid air which has formed, in such a way as to diminish the evaporation when it is evacuated.

Such is *compound liquefaction*, which possibly does not mark such an advance theoretically as liquefaction under pressure, but which presents additionally certain practical advantages of the same order as those which led to the compound expansion of steam.

One of these advantages is that relating to the diminution of harmful intervals. If the admission is very feeble, as is the case when it is desired to expand in one stage down to atmospheric pressure, the harmful interval involved is necessarily very large and the yield in liquid air is largely effected, as pointed out in our remarks in the note on p. 106. With compound expansion, on the contrary, the coefficient of admission into each cylinder is important, viz. about one fifth, account being taken of the considerable contraction during expansion, and the effect of the harmful interval becomes relatively insignificant.

In the method of construction adopted by Claude and represented diagrammatically in Fig. 54, it has been possible to endow these compound machines with other important practical advantages.

In machines with double action but single expansion such as are represented in Fig 51, two causes of diminished yield arise: from escapes from one face of the piston to the other through lack of tightness, and, on the other hand, from external escapes through the stuffing-box of the piston-rod. These latter are naturally much more serious than the others for equal amounts, because the cold of the corresponding air is completely lost and is equivalent to about half its weight in liquid air, while the air which passes from one face of the piston to the other is only lost from the point of view of the work it should have produced. *Per*

*contra*, the external escapes may be very slight in well constructed machines, so that finally it is the other cause which seems to predominate.

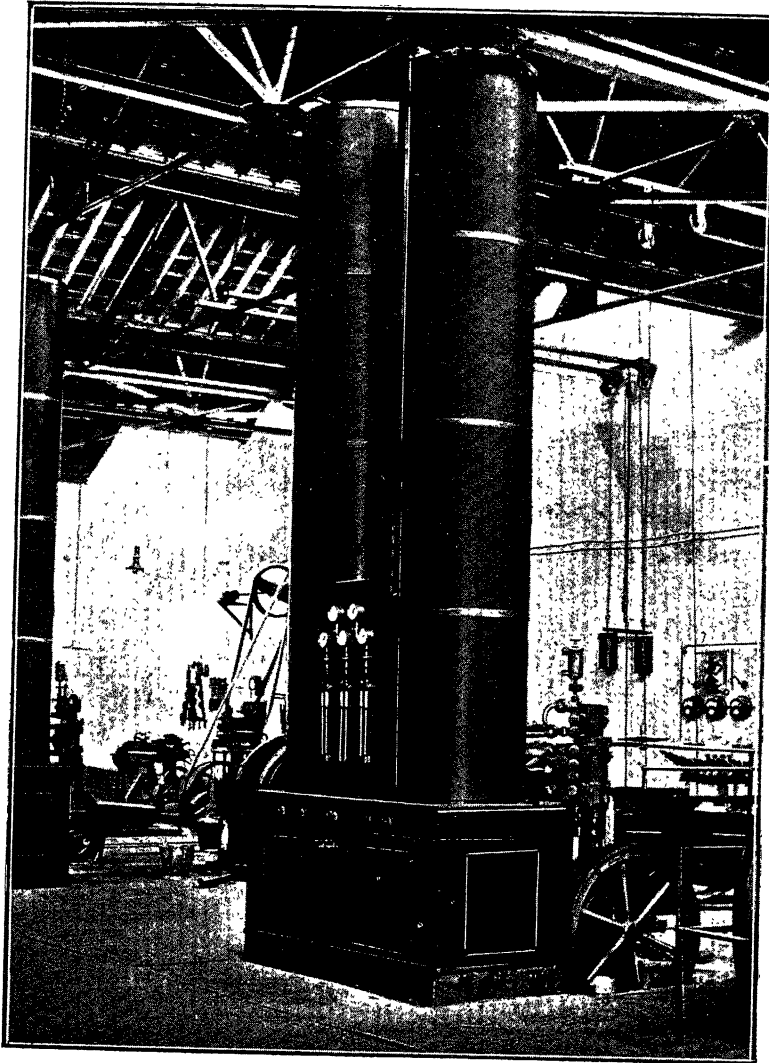


Fig. 55.—Compound machine for an output of 40 litres per hour coupled to one of the oxygen machines of the Liège Works.

Now Claude designed his compound machines by

used in expansion and working both with a single piston, as is shown on the diagram, and as can also be seen in the general elevation of the machine in Figs. 55 and 56, the machine being obviously single acting on top and able to be double or single acting at the bottom. This last case presents the advantage of permitting of a single system of governing the distribution for the two cylinders.

By this arrangement—

(1) The escapes through want of tightness in the high-pressure piston are entirely operative for the secondary expansion and are only lost to the primary.

(2) The stuffing-box of the piston has only to stand the feeble pressure of the secondary expansion, that is, 10 atmospheres at most, during admission, or even has only to support the pressure of the exhaust if the machine is equally single acting at low pressure.

Furthermore the lubrication with petrol ether is assured thanks to the inevitable lack of tightness in the high-pressure piston, by a single lubricator, fixed in this case, on the high-pressure cylinder itself.

The cumulative effect of these advantages is such that with this new advance an improvement has been noted, naturally not as great as the preceding, but amounting to at least 0.15 litres per H.P. hour, which has increased the yield, 1 machines using an over-all power of 75 H.P., by 0.85 litres per H.P. hour.

Fig. 55 represents a liquid air compound machine coupled to an oxygen apparatus of the capacity of 50 cubic meters per hour, and capable of producing 50 litres per hour; this requires an over-all power of 60 H.P. on the compressor shaft.

Fig. 56 represents a small unit especially designed for laboratories. Its capacity is of 5 litres per hour with over-all power of 15 H.P. It can be set working in thirty minutes.

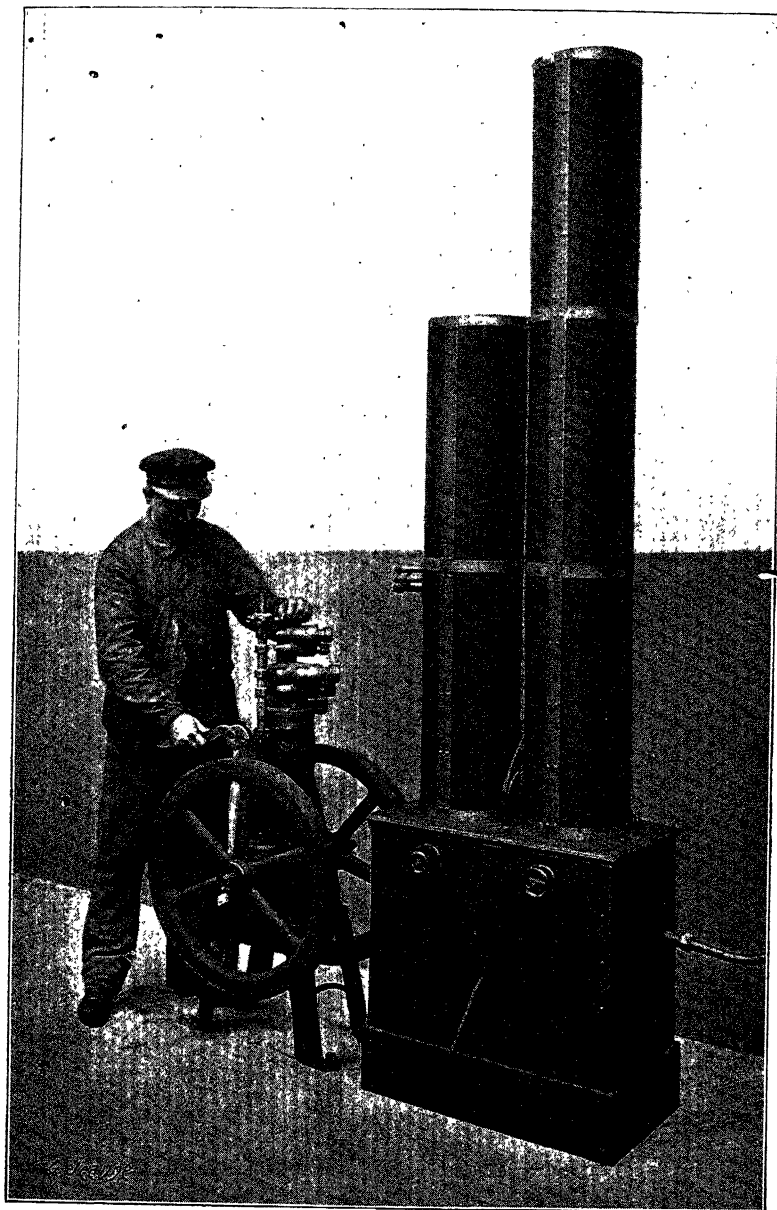


FIG. 56.—A liquid air unit—capacity 5 litres per hour, with compound liquefaction being erected. 1909.

Fig. 57 gives a diagrammatic representation of the theory of the plant—motive power, compression, desiccation, etc. The practical details are necessarily omitted.

As to the practical working of these machines, it will only be necessary to repeat what has already been stated, that is, that it is as easy and regular in working as a steam engine. In practice the workman in charge of running these machines has, so to say, only to look after the expander.

**Multiple expansion.**—In this way the essential condition for the production of cold by expansion with external works, that the expansion be wholly accomplished under suitable temperature conditions, that is, at the highest temperature compatible with the carrying out of liquefaction. We have seen that this is not the case, far from it, when matters are so arranged that liquefaction takes place spontaneously and completely, at the end of expansion; but that if liquefaction is effected under pressure, the commencement of expansion is improved, and that we obtain, through compound liquefaction, an immediate improvement in the expansion itself, thanks to the heating of the air before the end of its expansion.

It will be understood that nothing would prevent a further advance in this direction and a further improvement of the conditions, save the increasing complication of the parts, insufficiently compensated for by an ever-diminishing advantage owing to further fractionating the expansion, that through effecting it in three or four successive stages, each of them followed by liquefaction. We arrive thus visibly, in the limit, as we shall see presently, at an adiabatic expansion from  $-100^{\circ}\text{C.}$  to  $-140^{\circ}\text{C.}$ , and thereafter an isothermic expansion down to the end of the operation.

**Other remedies.**—Another means of utilising liquefaction under pressure may be used to avoid the defective state of matters which characterise the close of expansion, that is, to expand to the very end. It will be sufficient for this

object to operate in the same way as Linde by collecting the partially expanded air when issuing from the exchanger and recompressing it to its initial pressure. We could, for example, operate between 40 and 8 atmospheres. The work of compression for each kilogramme of air will thus be reduced from  $\text{Log } \frac{40}{1}$  to  $\text{Log } \frac{40}{8}$ , and as the work of expansion is reduced in a less ratio, since the end of the expansion from

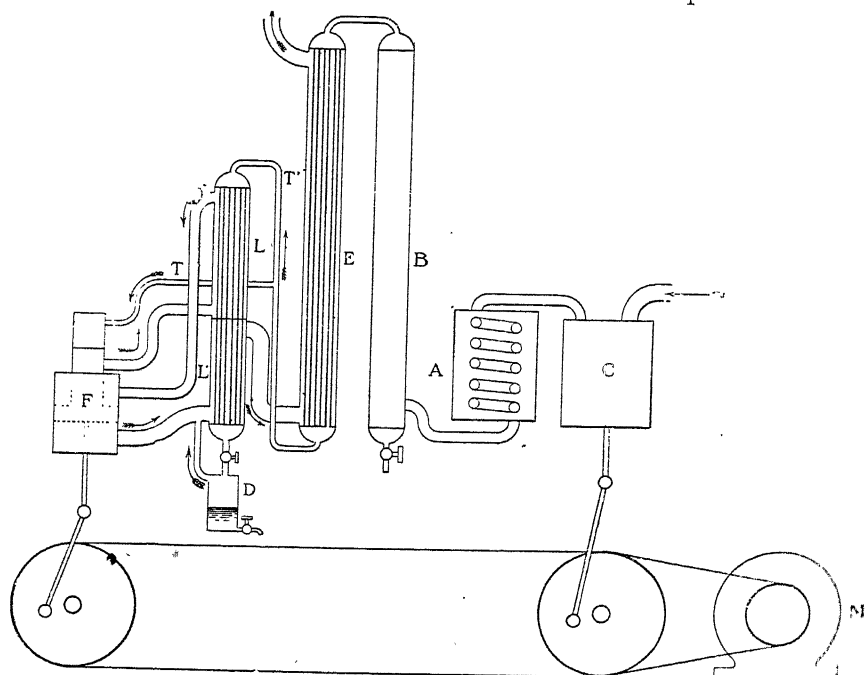


FIG. 57.—Theoretic diagram of an installation for liquid air with compound liquefaction.

40 to 1 is bad, the yield will be increased in comparison with this extended expansion. It will be objected, that the yield obtained from 40 to 8 is not very much better than that of complete expansion between 5 and 1, which would be much simpler. This is an error: there are at least three reasons why expansion from 40 to 8 should be practically better than expansion from 5 to 1.

(1) The working

to the pressure of 40 atmospheres, we are able to effect liquefaction at about  $-140^{\circ}\text{C}$ . instead of  $-170^{\circ}\text{C}$ . or  $-180^{\circ}\text{C}$ .

(2) The exchanges of temperature are better through being effected between gases under pressure.

(3) The effect of the internal work becomes in this case noteworthy, and constitutes a sensible addition. At 40 atmospheres this internal work, we know, is always per kilogramme—

$$\frac{a}{v_1} = \frac{12}{0.019} = 632 \text{ kilogrammeters or } 1.5 \text{ kilogramme calories (about),}$$

but instead of having to treat 6 kgs. of air per H.P. hour, as in the expansion from 40 to 1, equivalent to an addition of 9 calories derived from the internal work, the quantity of compressed air per H.P. hour from 8 to 40 amounts to about 13 kgs., which raises the gain due to internal work to 20 calories per H.P. hour. The gain amounts thus to 80 calories if we operate like Linde from 100 atmospheres, and expand as he does from 200 down to 50, and it might thus pay to add subsidiary cooling to further increase the addition.

Another advantage of this solution is the large reduction in the dimensions of the compressor.

This application of liquefaction under pressure is therefore very interesting in its application to the manufacture of liquid air; it is less so in the manufacture of gaseous oxygen, because in this case the air is not only the source of cold, but also that of the oxygen itself, and because all that which circulates in the closed cycle is lost to the object in view.

**Simple or compound expansion with liquefaction of oxygen under pressure.**—It has been shown by the progress realised above how important is the effect of the slightest change in the temperature of expansion. Now Claude thought of a means which promised, in addition to all the foregoing, to secure a new and important improvement.\*

\* French patent No. 322,107.



It will have been observed that in all the preceding devices, the temperature of the exhaust air was raised before its admission to the exchanger, as far as the temperature of liquefaction in the liquefier extended, or a little under, viz. to  $-140^{\circ}\text{C.}$  in the case of air subjected to its critical temperature. Now we know that oxygen is characterised by a critical temperature considerably higher than that of air, viz.  $-118^{\circ}\text{C.}$  If, therefore, a liquefier, and especially a compound liquefier, be fed no longer with air, but with oxygen at its critical pressure, the gain in temperature cannot be less than  $20^{\circ}\text{C.}$ ; the work of expansion will be considerably improved at the same time as the work of recuperation, considerably augmented, becomes available to offset the work expended in more appreciable measure, say 30 per cent. in a well-constructed machine.

Claude carried out in this connection some conclusive trials,\* substituting alternately air and oxygen in feeding the liquefier of a plant which, absorbed as in the preceding cases from 60 to 70 H.P., after deducting recuperation.

It being assumed that for *equal weights* the cold-producing values of liquid air and liquid oxygen are practically equal (the temperature of liquid air,  $-193^{\circ}\text{C.}$ , is lower than that of oxygen,  $-182.5^{\circ}\text{C.}$ , but the heat of evaporation, 49 calories, is less than that of oxygen, 51 calories), the outcome of these trials, expressed in terms of liquid air, shows in the case of oxygen a yield of 0.95 litres per H.P. hour as against 0.85 litres in the case of air. The improvement is therefore very clear. Theory (see further on) indicates that it should be still better under favourable conditions.

Now, the question is interesting, not only because of its theoretical interest, but because liquid air and liquid oxygen are concomitants of each other in the oxygen and

\* 'Proceedings of the Academy of Sciences' October 22nd 1904

nitrogen plants which constitute at the present day the most important applications of liquid air. There would be no difficulty in providing in such an apparatus what we may call the *supplementary liquid* (p. 315), under the form of liquid oxygen rather than under the form of liquid air.

It might, therefore, be of interest, in view of realised improvement, to feed the liquefiers in these plants with a supply of manufactured oxygen previously compressed down to the critical pressure. It should be remarked that we do not diminish, by so doing, the yield of useful oxygen, because all the oxygen taken from the oxygen plant to feed the liquefier is returned to that plant after liquefaction.

It is, in other words, a certain quantity of oxygen which circulates indefinitely in the same circuit, while the capacity for yield of the apparatus is not effected. We are only deprived of the additional oxygen furnished by the plant destined, if necessary, to feeding the liquefier, at the start of its compression.

#### ESTIMATE OF THE LIMITING YIELD OF EXPANSION WITH EXTERNAL WORK.

We now know what are the practical means which enable us to carry out expansion with external work, efficiently. It remains to carry out in this case what we have done in the case of expansion with internal work, and moreover, by means of the present practical results, the theoretical limit towards which more perfect construction of the erection of more powerful apparatus will enable us to attain.

To begin with, a possible objection should be dispelled. Let us recall this for a last time: the master idea of successive improvements described above, has consisted progressively raising the temperature of expansion up to the extreme limit compatible with liquefaction, so as to

abstract from the compressed air during expansion as much as possible of the energy which it contains. We have implicitly admitted, moreover, that all energy thus abstracted, in addition to the outside energy used, is transmuted into its equivalent in liquid air. Now this may not appear to be altogether self-evident; it might be thought that the degrees of cold thus produced are of inferior *quality* because of their temperature not being so low, and that for this reason they cannot be translated into degrees of cold at  $-190^{\circ}$  C. save with considerable loss.

One word will suffice to dissipate this fear. With perfect exchangers, the exhaust air escapes at the same temperature as the entering air without taking away any cold; therefore, all the cold produced must be represented under the form of liquid air, since this is the only form under which it does appear.

We have now to determine as exactly as possible the work of that portion of the air which is expanded.

We shall assume that it is to compressing this portion, that the work effectively expended is exclusively dedicated, and that the portion of the air which feeds the liquefier is compressed by means of the energy which is recuperated. This second portion represents, moreover, at most one quarter of the total quantity of air, so that the supposition in question is justified. We can, therefore, count upon 6 kgs. of air at 40 atmospheres being effectively expanded per H.P. hour.

The production of cold through the expansion of the air in a machine following after an exchanger of temperatures is obviously the result of the following circumstances, which may be estimated separately, on the supposition that conditions of temperature under which they are produced are the consequence of their united effect.

(1) *Internal work*.—We shall prove, as we have done in the case of Linde's process, that the quantity of this internal

work which intervenes in the yield of cold, is that which corresponds to the quantity of heat given out in the compressor owing to the internal pressure. The supplementary quantity given out in the exchanger does not count, and only leads to a fictitious increase in the fall of temperature at expansion. Under ordinary conditions of pressure in Claude's apparatus the addition due to internal work is, therefore, whatever the conditions of expansion may be, from—

$$\frac{12}{0.019} = 6.30 \text{ kgs. (about) or } 1.5 \text{ calories per kgrm. of air treated, or } 9 \text{ calories per H.P. hour.}$$

This addition is interesting, but also small enough to make it wholly unreasonable to wish to increase it by means of supplementary cooling. The cold-producing machine, indispensable to the Linde process, is here wholly superfluous, and the process thereupon makes up in simplicity for that which it lost through the substitution of an expansion machine for the expansion outlet.

(2) *Abnormal contraction of the compressed air and increase of volume of the expanded air in the exchanger.*—The initial  $pv$  of the compressed air at its admission to the exchanger is  $BO$  (Fig. 58), which, with the slight pressures used here, is inferior by  $AB$  to the  $pv$  of a perfect gas; this is an advantage, because the compressor in this way transmits,  $AB$  kilogrammeters less in the direction of the apparatus, and this is so much gained (this gain,  $AB$ , at 40 atmospheres and  $0^\circ \text{C.}$ , amounts to 170 kgms. or one third of a calorie per kilogramme). See in this connection generally Witkowski's table (p. 127).

In passing through the exchanger, the curve of contraction of the air at constant pressure,  $BN$ , diverges more and more from the *straight* line  $AM$ , which represents the contraction in a supposed perfect gas. This divergence becomes enormous when the temperature passes from

—130° C. to —140° C.,  $pv$  falling between these temperatures by one third of its value.

Let us consider the case where expansion takes place at the initial temperature  $T$ , represented in the figure by  $OT$ . The portion of the external energy,  $p_1 v_1$ , transmitted by the compressor and reaching to the expansion machine equals  $NT$ ; it is entirely absorbed (p. 103) by the work at full pressure. As to the portion of this energy given out abnormally in comparison with a perfect gas, viz.  $(LN—KM)$  or  $(MN—AB)$ , this has its counterpart in the absorption of heat corresponding to the work of increase

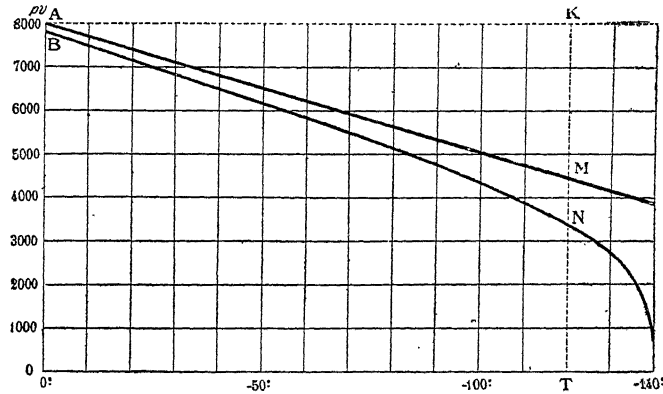


FIG. 58.—Anomalies of the contraction of compressed air in the exchanger. (The draughtsman has omitted  $BL$  parallel to  $AK$  cutting  $KT$  at  $L$ .)

of volume in the expanded air from the temperature at the end of expansion  $T'$  to that of beginning of expansion  $T$ .\* If this counterpart does not equal at least to  $(MN—AB)$ , the loss will have to be made good at the expense of a portion of the work of expansion. Now this is just what takes place at —140° C., where, according to Witkowski's table,  $MN=2992$  kgms. per kilogramme,  $AB=170$ ,  $(MN—AB)=$  about 2800 kgrm., while the counterpart work of

\* The remainder of the work of increase of volume in this expanded air from  $T$  to the temperature of the environment equivalent in its capacity in a sensibly perfect gas to the "normal" portion of work of contraction in the compressed air (see p. 144 for same reasoning).

increase of volume from  $-190^{\circ}\text{C.}$  to  $-140^{\circ}\text{C.}$  represents only 1400 kgms.

There is therefore a loss of 1400 calories, or 3.3 calories per kilogramme, to *deduct* from the effect of an expansion which is in itself detestable.

On the contrary, when the expansion takes place at  $-103$  (in the case of liquefaction under pressure), we have, according to Witkowski,  $MN = 880$ ,  $AB = 170$ ,  $(MN - AB) = 710$ ; therefore the counterpart, represented by the work of increase of volume from  $-140^{\circ}\text{C.}$  to  $-103^{\circ}\text{C.}$ , is not less than 1100 kgms., equal to a *bonus* of 400 kgms. or 1 calorie per kilogramme to *add* to the effect of the expansion itself, estimated further on.

*Work of expansion.*—It would evidently be very difficult to frame and solve the equations for expansion, which is half *adiabatic* and half *isothermic* with the variations in specific heat which occur in this connection. We shall again have to proceed by the graphic method, constructing the curve of  $p$  as a function of  $v_1$ , measuring the area subtended by this curve, and deducting the part under full pressure which compensates for the portion of  $p_1v_1$  which is delivered to the machine. The sum of the result obtained of the internal work and of the positive or negative effect of paragraph (2) will give the total yield in cold, of the operation.

To construct in the first place the curve relating to  $-140^{\circ}\text{C.}$  admission at 40 atmospheres (the case of spontaneous liquefaction), we have seen, according to Witkowski, the initial volume at 40 atmospheres (a very small volume) is—

$$v_1 = \frac{904}{10,330 \times 40} = 0.00219m^3,$$

which gives us the point  $R$  (Fig. 59).

Starting from this point the form of the curve is determined by the fact that the expansion of the quasi-liquid which now arises in the machine involves a very deep fall in the temperature and an abundant liquefaction,

followed by re-evaporation in the inverse circulation, so that the curve of pressure must fall almost vertically starting from  $P$ . When, for example, the volume has become ten times the initial volume, or  $v = 0.07 m^3$ , the pressure is certainly not more than the twentieth of the initial pressure, or 2 atmospheres. These considerations account for the form of curve indicated.

The area resulting therefrom, which represents the total external work, is very small, being at most 4500 kgms.

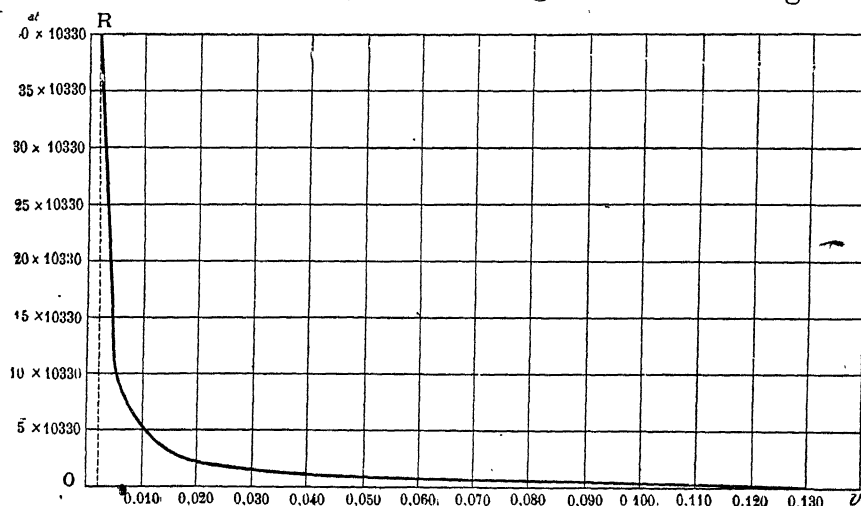


FIG. 59.—Work of expansion in the case of spontaneous liquefaction.

When we have deducted therefrom the part under full pressure, that is,  $p_1 v_1 = 904$  kgms., then the 1400 kgms. required above to compensate for the portion of  $(MN-AB)$  which is not neutralised by the work of increase of volume in the expanded air, there remains for the useful effect of the external work 2200 kgms., or 5 calories per kilogramme. Adding thereto the 1.5 calories per kilogramme corresponding to the work of internal pressure carried out at the ordinary temperature, we arrive at the total effect of 6.5 calories per kilogramme, or **40 calories per h.p. hour.**

This is much less than in Linde's perfected expansion,

and it is not astonishing that Claude's first results should have been so bad.

Let us consider on the contrary the most favourable case of liquefaction with air under pressure, that is, the limiting case where the initial temperature being about  $-100^{\circ}\text{C}.$ , is rapidly lowered down to  $-140^{\circ}\text{C}.$  in consequence of the lowering of the specific heat and of the effect itself of expansion, the latter being continued thereafter isothermically while provoking the liquefaction of the air at the critical

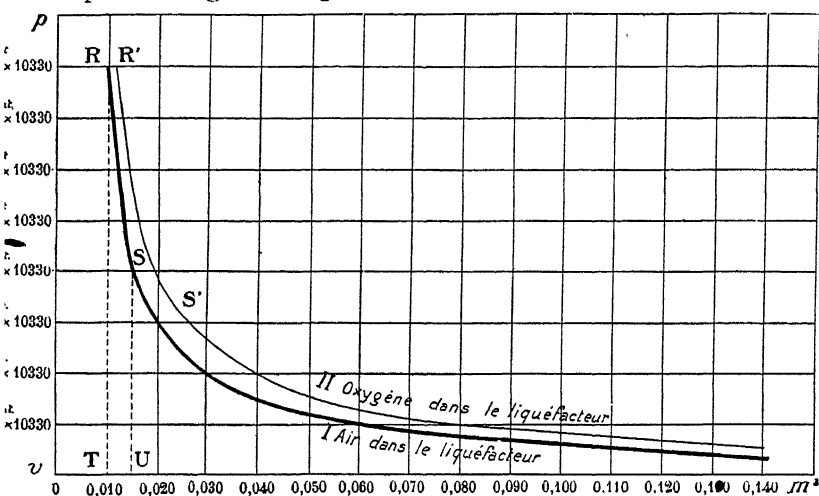


FIG. 60.—Work of expansion, limiting case of isothermic expansion; I with air in the liquefier; II with oxygen in the liquefier.

pressure. Here the initial volume is enormous in comparison to the preceding case. It is, according to Witkowski (taking  $-103^{\circ}\text{C}.$  as the initial  $T$ ),

$$v_1 = \frac{4104}{40 \times 10,330} = 0.010m^3,$$

corresponding to  $R$  (Curve I, Fig. 60).

We are going to investigate to what value the pressure must fall to enable the temperature of  $-140^{\circ}\text{C}.$  to be attained, and we shall premise that from this pressure up to the atmospheric pressure, the isothermic expansion is effected according to the formula for a perfect gas,



which is very much *inferior* to the reality, as our imperfect gas has to dilate itself, from this temperature of  $-140^{\circ}\text{C}$ . much more than is indicated by Mariotte's law. Now, the pressure at which the temperature reaches  $-140^{\circ}\text{C}$ . is certainly lower than 30 atmospheres, for according to Witkowski's second table at 30 atmospheres and  $-140^{\circ}\text{C}$ . the value of  $pv = 2448$ , hence—

$$v = \frac{2448}{30 \times 10,330} = 0.008,$$

and the volume, which was at starting 0.010, cannot diminish.

It falls, therefore, to at least 20 atmospheres, because at 20 atmospheres and  $-140^{\circ}\text{C}$ . we get,

$$pv = 3048, \text{ that is, } v = \frac{3048}{20 \times 10,330} = 0.015,$$

which represents only the slightest increase of volume,  $TU$  (Fig. 60).

Lét us calculate the area of Curve I under this hypothesis. The isothermic expansion of from 20 down to 1 atmosphere produces at  $-140^{\circ}\text{C}$ .—

$$pv \log_e 20 = 3048 \log_e 20 = 9144 \text{ kgms.},$$

which represents the surface of the curve to the right of  $SU$ . Besides this, the work under full pressure being only that to the left of  $RT$ , we have still to add as work of expansion the surface  $RSTU$ , which can easily be calculated on the supposition that  $RS$  is a straight line.

$$RSTU = \frac{40 + 20}{2} \times 10,330 \times 0.005 = 1550 \text{ kgms.}$$

Therefore—

$$\text{Total work of expansion} = 9144 + 1550 = 10,694 \text{ kgms.}$$

We have seen that in this case the counterpart of ( $MN-AB$ ) is greater by 400 kgms. per kilogramme, so that the external total work amounts thus to 11,000 kgms., or 26 calories per kilogramme, to which must be added the 1.5 calories per kilogramme of the internal work, that is, a total

f 28 calories per kilogramme or 168 calories per H.P. hour. but we have drawn attention to the fact that this result gives too modest idea of the yield, because air, when expanded at  $-140^{\circ}\text{C}.$ , expands far more than a perfect gas. A striking proof of this insufficiency is furnished us if we suppose that the temperature of  $-140^{\circ}\text{C}.$  is only attained at 15 atmospheres, and that it is only from this pressure that the expansion assumed to be isothermic is produced. Such an eventuality would manifestly correspond to far less work of expansion from 15 to 1 than from 20 to 1, as previously. If, however, we make the calculation, we shall find very early as much, and this because we start at 15 atmospheres from a volume given without hypothesis by Witkowski's table. Here, moreover, the initial volume being always—

$$v_1 = 0.010,$$

the real volume under the pressure of 15 atmospheres, according to the table, is—

$$\frac{3280}{15 \times 10,330} = 0.0213.$$

whereas, calculated from the preceding curve, it was barely 0.020 under this same pressure.

The isothermic expansion at  $-140^{\circ}\text{C}.$  from 15 to 1 atmosphere brings into play—

$$pv \log_e 15 = 3280 \times 2.69 = 8.829,$$

or a slight diminution of 300 kgms. on the 9144 which we got above.

On the other hand, *RSTU* gives in this case—

$$\begin{aligned} 27.5 \times 10,330 \times 0.0113 &= 3210 \\ \text{Therefore total work of expansion} &\underline{12,089} \end{aligned}$$

add excess of work of dilatation over (*MN-AB*),

$$\begin{aligned} \text{Viz. } &400 \\ \text{Total } &\underline{12,489} \text{ kgms.} \end{aligned}$$

or 29 calories per kilogramme.

To this must still be added the 1.5 calories per kilogramme of the internal work, which bring up the final total to 31 calories per kilogramme, or 186 calories per H.P. hour.

**Quantity of energy recuperated.**—As to the quantity of energy recuperated and capable of coming to the assistance of compression, and of furnishing, according to our hypothesis (p. 191), the portion of the compressed air which feeds the liquefier, it is evidently equal to the total area of the expansion curve, inclusive of the work under full pressure. This total surface represents 15,600 kgms. per kilogramme of expanded air, that is, per the 6 kgms. furnished per H.P. hour at the pressure of 40 atmospheres, 93,600 kgms. theoretically saved per H.P. power expended, which is sufficient to justify the hypothesis.

**Case of feeding the liquefier with oxygen.**—The same calculations have been made in the case where oxygen is used in the liquefier, corresponding to an initial temperature of  $-85^{\circ}$  C. and to an isothermic expansion starting from  $-118^{\circ}$  C. only; these are shown with Witkowski's results interpolated in the curve  $R'S'$  drawn with a thin line (Fig. 60), and a theoretical limiting yield of 40 calories per kilogramme, or 240 calories per H.P. hour.

This is—apart from improvements in the appliances for the compression of the air—the maximum which it is possible to obtain in the direction in question.

**Other investigations on expansion with external work.**—Before ending this chapter it will be useful to describe the investigations carried out independently of Claude into the practical realisation of expansion with external work. These, however, amount to very little.

Ostergreen and Burger in 1901 devised a system for working the mechanical expansion of air. This system is described in the 'Bulletin de la Société d'Encouragement,' 1902. Fig. 61, which gives the details of the expander

alone, shows that this machine could not with good grace lay any claim to simplicity. No special device is indicated to ensure lubrication. Now, to raise the temperatures, the liquefaction of the air as far as expansion is concerned is effected spontaneously.

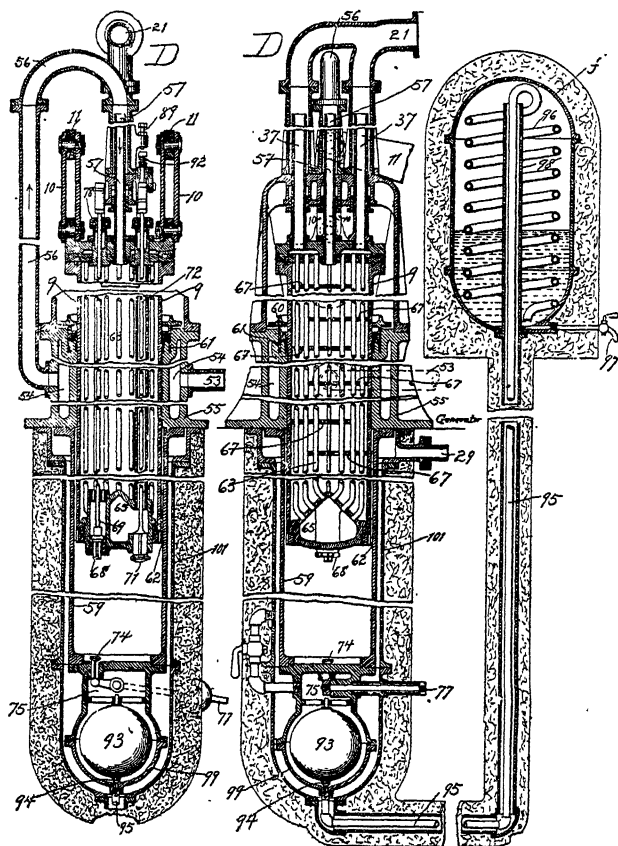


FIG. 61.—Ostergreen and Burger's expander.

From these facts it is easy to deduce suitable conclusions as to the output capacity of this machine.

Pictet\* carries out the expansion of the compressed air in a machine inclined at an angle of  $45^\circ$ , lubricated by

\* French patent 324,715 of September 24th, 1902.

means which are indicated and cooled down to the temperature of liquid air before being started (see p. 160).

The essential feature of the patented process is to expand air completely freed from all traces of carbonic acid and circulating indefinitely in the same circuit, because this carbonic acid, by accumulating in solid lumps on the faces of the pistons, gives rise to accidents of which the author, in his patent, gives a very impressive description. We do not believe that Pictet observed anything analogous hereto; in Claude's machines when he paid a visit to his works in August, 1902—a simple exchange of courtesies—a few days after the visit of the Committee of the Academy of Sciences (p. 165).

Such a device is not in other ways calculated to give acceptable results unless combined with liquefaction under pressure.

This machine was shown in 1906 at the Milan exhibition as the *first* piston machine which worked at the temperature of liquid air—a simple *lapsus calami* surely, for Pictet must have intended to say the *second*.

Place, who has been studying the question since 1905, and whose methods have been tried at Norwich (U.S.A.) by the *New England Refrigerating Company*, has also availed himself of a piston machine. This inventor, however, applies liquefaction under the critical pressure without any discretion, but with the pretext that at this pressure liquefaction is much more abundant because the heat of the liquefaction is *nil*; he has reason to flatter himself so much on account of this happy borrowing, that he jumps with feet together over all theory, and obtains neither more nor less than 3.5 litres of liquid air per H.P. hour.

# PART III

## PRESERVATION AND PROPERTIES OF LIQUID AIR

### CHAPTER VIII

#### PRESERVATION OF LIQUID AIR

WE are now in a position to produce liquid air in unlimited quantities. Before proceeding further, it appears to us to be necessary to speak a little of its properties, and to begin with, to describe how it is preserved.

**A difficult problem.**—Difficult, certainly! To such a degree that although it is solved at the present time, so to speak, perfectly from the scientific point of view, it is so badly solved, practically speaking, that liquid air has seen its industrial applications cut down to the single case where it can be used as and when it is produced. This case is happily that of its most essential applications, to wit, in the manufacture of oxygen and nitrogen.

Here in this beaker, of a somewhat special shape (Fig. 62), is some liquid air. It is a limpid liquid resembling water, and, like it, undisturbed. And you observe, not without astonishment, we presume, with what ease it can be manipulated in the free air, transferring it from one beaker to another exactly as if it were water, or at most, boiling water. At first sight this seems to be a paradox!

Produced under such excessive conditions of temperature and pressure, it would appear certainly that as soon as the liquid air is in contact with free air, nothing could be in a greater hurry to resume the gaseous state from which we have had such trouble to snatch it.

Nevertheless, you can see that it is nothing of the kind.

Why?

Let us take some gaseous air and cool it down to its critical temperature, that is  $-140^{\circ}\text{C}$ . At this temperature we know by experience this air is capable of being liquefied, but to achieve this a considerable pressure is required—that is, 40 atmospheres.

Now, instead of cooling the air exactly to  $-140^{\circ}\text{C}$ ., let us cool it a little more, for example to  $-150^{\circ}\text{C}$ . It is evident that this colder gas will be on that very account more easy to liquefy, and that a more feeble pressure, say—24 atmospheres, will be sufficient for the purpose.

In other words, to each temperature starting from  $-140^{\circ}\text{C}$ . corresponds a pressure capable of liquefying the air so much the lighter that the temperature is lower. By persevering along this road, and by cooling more and more, we must arrive, and we shall arrive, in point of fact, to a sufficiently low temperature to cause the air to liquefy under the pressure of 1 atmosphere, *that is, under the effect of atmospheric pressure alone*.

This result is brought about when the temperature is lowered to  $-193.5^{\circ}\text{C}$ .

And if at this temperature gaseous air is liquefied at atmospheric pressure, the liquid air which has been already produced would be extremely ungracious if it declined to remain in that form when its temperature is actually  $-193.5^{\circ}\text{C}$ .

Therefore—first point—the existence of a high pressure on liquid air is not indispensable to its preservation; ordinary atmospheric pressure will suffice, and conse-

### *PRESERVATION AND PROPERTIES OF LIQUID AIR*

ently the use of open recipients is possible to preserve provided that the temperature of the liquid be maintained at  $-193.5^{\circ}\text{C}$ . Now we shall see that by the simple play of well-known physical laws, the temperature of liquid air exposed to the free air regulates itself exactly  $-193.5^{\circ}\text{C}$ .

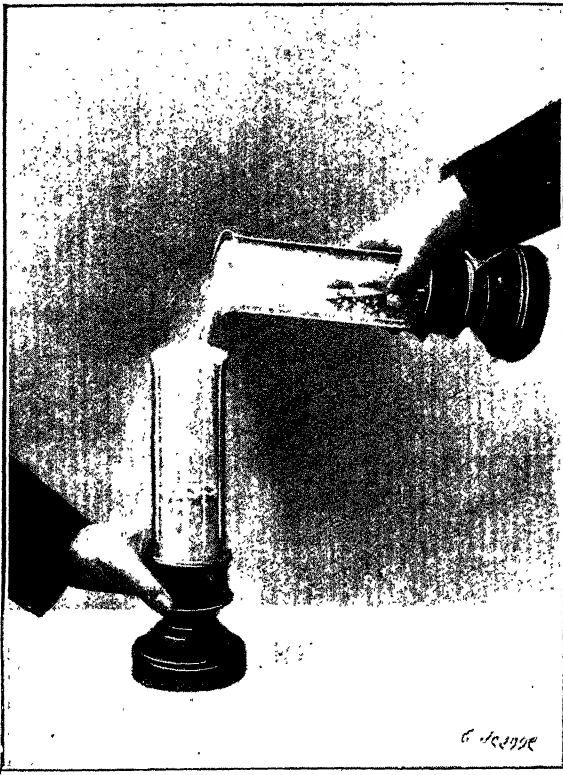


FIG. 62.—Manipulation of liquid air in free air.

Let us place water on a very hot hearth. After a few seconds it begins to boil and is evaporated away; but the hearth may be as hot as you like, and we find that the portion which remains liquid until complete evaporation will not exceed  $100^{\circ}\text{C}$ ., the temperature of boiling water under atmospheric pressure (p. 7).



Now this is a general law of physics, and applies to all liquids. And liquid air, left to itself in the ordinary environment, which is relatively a *veritable furnace* in temperature, will behave exactly as water did on the hearth referred to above. It will rapidly evaporate till complete

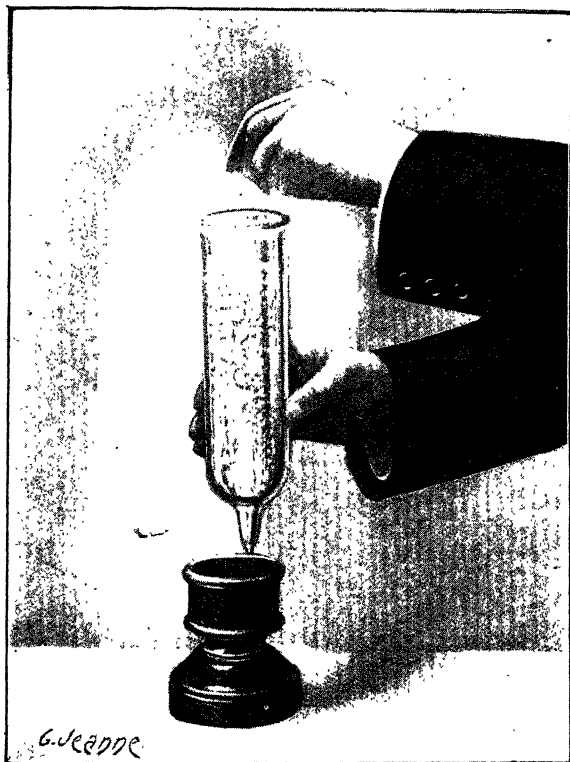


FIG. 63.—Violent ebullition provoked by a piece of chalk dropped into liquid air.

evaporation; the liquid portion will remain immovably at its boiling temperature under atmospheric pressure, viz.  $-193.5^{\circ}\text{C}$ .

This is, moreover, the case for all liquids whose ebullition is produced at a temperature inferior to the surrounding temperature, that is for all liquefied gases which in the

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the air correspond to no other temperature than that of air boiling point.

Thus the temperature of the liquid air contained in an open recipient is inevitably  $-193.5^{\circ}$ , save some slight variations consequent upon the respective proportions of oxygen and nitrogen. This is the second point determined.

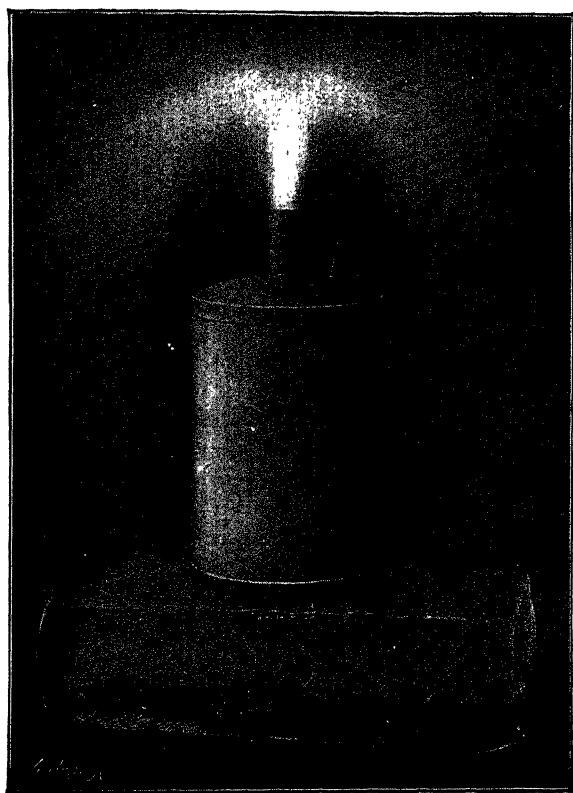


FIG. 64.—“The magic kettle.”

On the other hand, as has just been stated before, our liquid left to itself would evaporate rapidly. But this, however, requires some qualification.

When a liquid evaporates, it absorbs heat (p. 6). This is also a general law of physics, and liquid air is no

more independent thereof than it was in the preceding case.

Certainly this heat which it requires for evaporation is not difficult to obtain, since because of the enormous excess of the temperature of the environment over that of

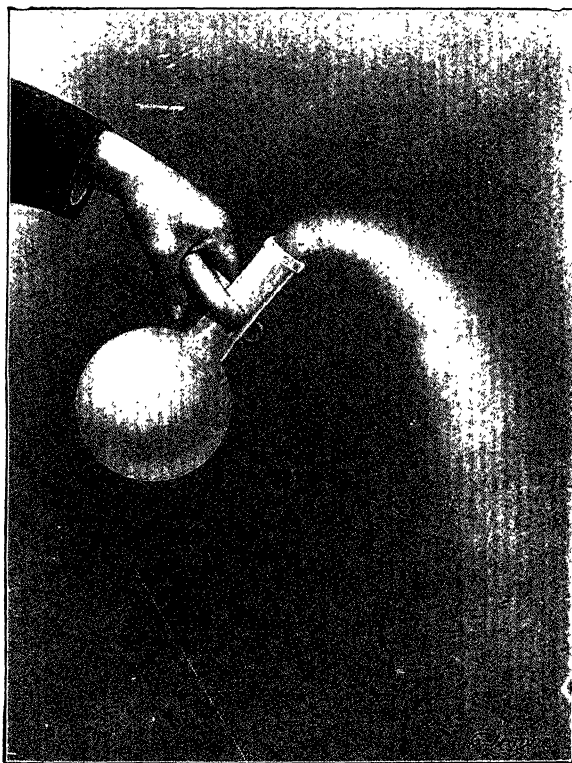


FIG. 65.—Rapid evaporation of liquid air in a naked flask.

the liquid air, all surrounding bodies are *burning* in comparison therewith. Let us throw a piece of anything—say of chalk—into the liquid air, and it at once begins to boil violently (Fig. 63) till the piece of chalk is cooled down to  $-190^{\circ}\text{C}$ .

There is even something more remarkable in this connection: you will remark that the burning body when compared

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th the liquid air might very well be a *piece of ice* instead of chalk, whose  $0^{\circ}\text{C.}$  cuts a very poor figure when compared with the  $-190^{\circ}\text{C.}$  of the liquid air. Therefore, if we place a block of ice in a recipient containing liquid air, the latter will begin to boil violently. This is called in "music hall" phraseology making water boil with ice: this is the *magic kettle* of celebrated memory (Fig. 64).

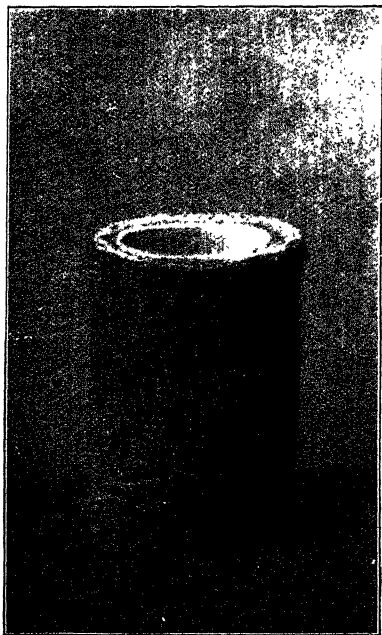


FIG. 66.—Recipient for liquid air covered by an imperfect coat of insulating material.

If, therefore, the heat of the environment is able to penetrate without difficulty to the liquid air, its evaporation will in practice be very rapid. This is the case with the liquid air contained in the flask, which is not protected in any way from the heat of the environment (Fig. 65), and you can see in practice how rapid the evaporation is by the look of the thick white smoke which escapes therefrom,

and is the usual accompaniment of experiments with liquid air. Let us remark in passing that the smoke is cold—very cold—in spite of its appearance of steam from boiling water. We ought not, however, as is too often the case, to take it for liquid air smoke. It arises quite simply from the instantaneous condensation of impurities in the atmosphere, moisture and carbonic acid.

Another part of this moisture, moreover, is deposited on the sides of the flask, as shown in Fig. 66, in a layer of rime which is rapidly thickened.

We can now see very well where lies the fault in our previous enunciation: the rapidity of evaporation of the liquid air is not *unavoidably* very great; it depends *entirely* upon the rapidity of communication of the external heat. Supposing we could entirely obstruct the penetration of this heat of the environment. Then the liquid air, however essentially volatile it may appear to us, would find it wholly impossible to evaporate, since to do this heat is required, *and it will be preserved indefinitely.*

**First means of slowing down evaporation.**—Only, it is indispensable to be convinced, that if our idea is easy to define, it is far less simple to apply. Some idea of the difficulty may be gathered from the remark that to try and preserve liquid air at ordinary temperatures, during one week, is—a little less easy than attempting to preserve for a similar time a few litres of water inside a furnace heated to a red heat.

We may be able without difficulty to slow down the evaporation of liquid air by surrounding the recipients containing it, with bodies which are bad conductors of heat—cork powder, wool, felt, etc. (Fig. 66).

By wrapping them up thus with greater care still than we take in covering ourselves in winter with thick wraps and furs, it will appear that we aim exactly at an opposite goal: instead of preventing the heat from going out, we aim at

## PRESERVATION AND PROPERTIES OF LIQUID AIR

venting it coming in. Strange paradox! The very heavy coats with which we cover these recipients are intended to prevent their *catching heat*. The paradox, however, is only apparent; it reminds us that the qualification of *very warm* applied to our winter clothes has no existence in fact, and that if we do not possess in our body itself a source of heat always active, the thickest possible clothes that could be obtained would not warm us. For liquid air in any case the climate is not very favourable. It takes all the trouble in the world to manage to keep some liquid air for one day in a recipient of 20 litres capacity which is thus protected.

Happily, there are better means.

**D'Arsonval's process; recipients with double walls and a vacuum between.**—A much more elegant as well as infinitely more efficient device has been discovered ever since 1887 by d'Arsonval, the well-known French scientist, and perfected by the English scientist, Dewar.

This process is based upon a knowledge of the fact that the penetration of heat calls into play two distinct modes of action, and consists in barring the way to each of these by appropriate means.

The first method of transmission by means of which heat can penetrate to the liquid air is transmission by *conductivity*. It is the method by means of which a metal plate placed in a fire is soon burning hot at the opposite end. It is a method of transmission from molecule to molecule which uncompromisingly implies the existence of continuity of material bodies, solid, liquid, or gaseous, these last acting more specially by *convection*, that is, by the transference of heat by gaseous molecules passing alternately from a hot body to a cold body, and *vice versa*. Hence, if we provide a space in the thickness of the walls of the recipient which the heat of the environment must pass to reach the liquid air, and which is entirely deprived of these material molecules, that is, in which we shall have

produced a perfect *vacuum*, we shall have opposed an absolute obstacle to this first mode of propagation.

D'Arsonval has very ingeniously availed himself of this fact, the knowledge of which slumbered uselessly in the treatises on physics ever since the investigations of

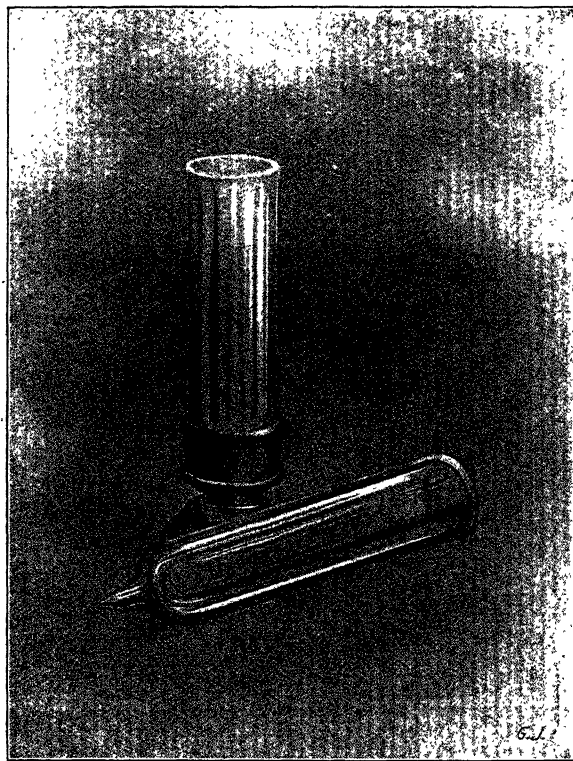


FIG. 67.—D'Arsonval recipients with double walls and internal vacuum.

Dulong and Petit. He made (Fig. 67) some recipients with double glass envelopes, which formed a hollow wall inside which as perfect a vacuum as possible was made through the point at the bottom, which was afterwards sealed with the blow-pipe. The evaporation of the liquid air contained in recipients thus fashioned finds itself already enormously slowed down.

## 2 PRESERVATION AND PROPERTIES OF LIQUID AIR

It was in 1887 that d'Arsonval devised this elegant application.

Doubtless there was no question in his mind of preserving liquid air in suchlike recipients, as liquid air at that time was not yet being handled save in minimum quantities in certain privileged laboratories. It is none the less true, however, that the first application of these recipients, for which purpose they were indeed devised, was precisely to hold without fear of sensible evaporation another liquefied gas—*chloride of methyl*, which is frequently used as an anæsthetic by surgeons.\* As d'Arsonval states with infinite reason, the double-wall recipients with internal vacuum have been realised both as to form and use ever since 1887. If the description, strictly speaking, is reasonable in England, it is distressing in France to constantly hear these recipients called Dewar's cups.

The illustrious English scientist certainly devised, as far back as 1874, a calorimeter to which he applied the insulating properties of a vacuum to avoid the causes of error arising from the penetration of heat. But what shows the two objectives to have been very different, is that when manipulating liquefied gases at the laboratory of the Royal Institution during a series of memorable investigations continued ever since 1883, although exposed to continual difficulties through their rapid evaporation; though Dewar was the first to think of using suchlike recipients for liquefied gases, he did not actually do so till 1892, that is, not till nine years after the very complete description given of them by d'Arsonval.

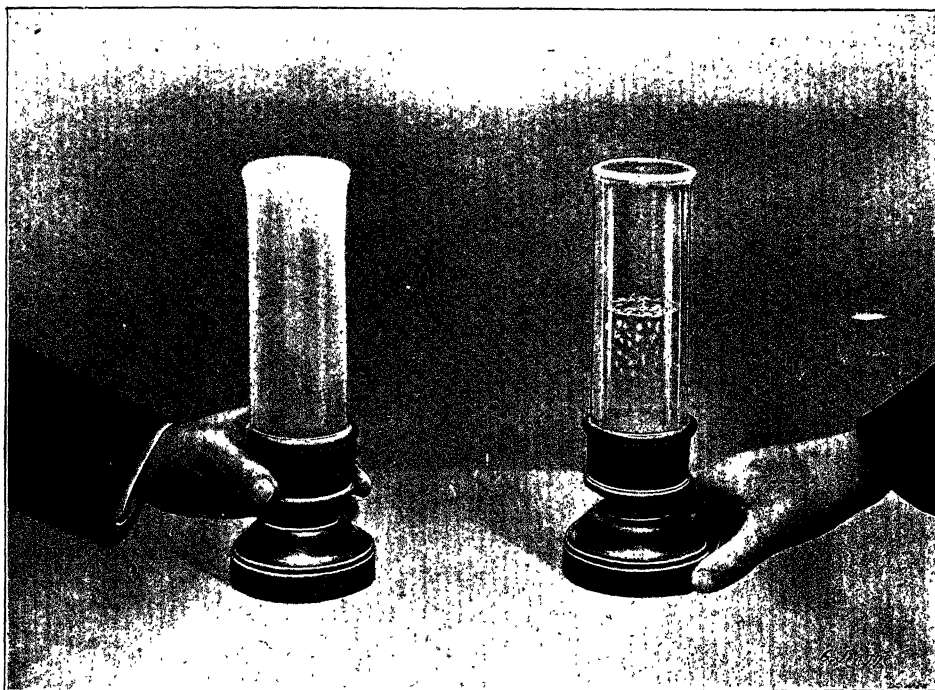
Notwithstanding everything, the recipients thus manufactured are still very far from being sufficiently efficient, difficult is the preservation of this extraordinary liquid. Evaporation is only reduced thereby, in the litre size of recipient, to about *one tenth* of what it was in the recipient

\* 'Proceedings of the Biological Society of France,' February 11th, 1888.



which was not protected at all—and this is far too little. Here (Figs. 68 and 69) is a beaker of this kind which is filled with liquid air.

After the agitation at starting has calmed down, you will see numerous bubbles continually rising in the liquid and rapidly increasing in size, which are nothing more than



FIGS. 68 and 69.—Insufficiency of the vacuum alone as a means of protection against heat. The liquid boils briskly, and after an instant the cup becomes cloudy and covered with rime.

bubbles of vaporised liquid air exactly analogous to the bubbles of water-vapour when boiling. Wait a minute and you will see the external walls of the recipient get covered with mist, and then, especially if the temperature is low, with beautiful arborescent figures similar to those which winter produces on the windows of our apartments,

## PRESERVATION AND PROPERTIES OF LIQUID AIR

d which by their occurrence furnish another indication the still too rapid evaporation of the air.

It signifies that, in point of fact, the means devised by Arsonval only places an obstacle in the way of the trans-  
sion of heat by conduction, and that heat can also propa-  
te itself by a second means very different from the first.

Furthermore, it must needs be thus, for if heat had at  
disposal no other means of diffusion than conduction,  
e sun could not warm the earth, separated therefrom by  
e boundless and perfect vacuum of the interplanetary  
ace. Now, we know that a metallic surface exposed to  
e sun becomes burning hot, much better than the sur-  
rounding air: it cannot be the air which yields its heat  
ereto since it is the cooler of the two. This abnormal  
ating is due to the heat directly transmitted by the sun  
der the form of *heat-rays*, which are completely analogous  
rays of light.

All hot bodies—and it should be added all bodies which  
round us, even ice, even carbonic acid snow, are  
atively hot, and therefore emit, like the sun, heat-rays  
able of warming *bodies colder than themselves*—it is this  
liant heat which penetrates without obstacle to the  
uid air across the transparent walls of the d'Arsonval  
ipients. This easy passage of the radiant heat can be  
own in a very striking manner in the beautiful exper-  
nt which we shall describe later, and which consist in  
nging about the very energetic combustion of an arc-  
p carbon in liquid oxygen enclosed in a d'Arsonval  
t-tube. If we approach our hand thereupon to this  
ipient, filled with a liquid at  $-180^{\circ}\text{C}.$ , we feel, so  
ndant is the radiant heat crossing the vacuum space, a  
sation of heat approaching almost to burning.

It is this easy passage of radiant heat which causes the  
uid air to evaporate with much too great a rapidity in  
s case, although evaporation is already ten times less

than when conductivity was free to act. This residual penetration is disastrous, as it prevents us on its account alone, from preserving for more than one day, the liquid air contained in a one-litre recipient.

**Dewar's improvement: Silvered vacuum recipients.—**

Thus notwithstanding the happy adoption of Dulong and Petit's idea, we should be far from well advanced in the problem of preserving liquid air were it not that by a curious coincidence other work of the same scientific men was there most conveniently available to show us the means of barring the road to radiant heat in its turn, and to reduce almost to nothing the residual transmissibility which is already so slight in the d'Arsonval recipients.

Dulong and Petit, however, have demonstrated that the *capacity for radiant* transmission of the wall of a vessel varies greatly with the character of its surface. A white, brilliant surface at equal temperatures radiates much less heat than a dark and dull surface. The blackened cast-iron stove of the workman's dwelling would heat far better than the porcelain stove of the middle-class home if the coal was not unfortunately supplied too parsimoniously thereto. We dress in summer in white clothes, because these form a kind of screen against the solar rays instead of radiating the heat they receive towards our bodies.

Hence arose Dewar's idea. Let us give unto Dewar what pertains unto Dewar—of completing d'Arsonval's very happy conception by *silvering* the internal surfaces of these recipients with double walls and intermediate vacuum—an idea, so much the more practical in that we know with what ease glass can be silvered, thanks to the reducing action of the introverted sugars on the solutions of silver salts.\*

These are the recipients shown here (Fig. 70)—a triumph of the glass-blower's art, because, as can well be imagined, it

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#### 4 PRESERVATION AND PROPERTIES OF LIQUID AIR

and which by their occurrence furnish another indication of the still too rapid evaporation of the air.

It signifies that, in point of fact, the means devised by Arsonval only places an obstacle in the way of the transmission of heat by conduction, and that heat can also propagate itself by a second means very different from the first.

Furthermore, it must needs be thus, for if heat had at its disposal no other means of diffusion than conduction, the sun could not warm the earth, separated therefrom by the boundless and perfect vacuum of the interplanetary space. Now, we know that a metallic surface exposed to the sun becomes burning hot, much better than the surrounding air: it cannot be the air which yields its heat hereto since it is the cooler of the two. This abnormal heating is due to the heat directly transmitted by the sun under the form of *heat-rays*, which are completely analogous to rays of light.

All hot bodies—and it should be added all bodies which surround us, even ice, even carbonic acid snow, are relatively hot, and therefore emit, like the sun, heat-rays capable of warming *bodies colder than themselves*—it is this radiant heat which penetrates without obstacle to the liquid air across the transparent walls of the d'Arsonval recipients. This easy passage of the radiant heat can be shown in a very striking manner in the beautiful experiment which we shall describe later, and which consists in lighting about the very energetic combustion of an arc of carbon in liquid oxygen enclosed in a d'Arsonval test-tube. If we approach our hand thereupon to this recipient, filled with a liquid at  $-180^{\circ}\text{C}.$ , we feel, so abundant is the radiant heat crossing the vacuum space, a sensation of heat approaching almost to burning.

It is this easy passage of radiant heat which causes the liquid air to evaporate with much too great a rapidity in this case, although evaporation is already ten times less

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## 2. PRESERVATION AND PROPERTIES OF LIQUID AIR

It was in 1887 that d'Arsonval devised this elegant application.

Doubtless there was no question in his mind of preserving liquid air in suchlike recipients, as liquid air at that time was not yet being handled save in minimum quantities in certain privileged laboratories. It is none the less true, however, that the first application of these recipients, for which purpose they were indeed devised, was precisely to hold without fear of sensible evaporation other liquefied gas—*chloride of methyl*, which is frequently used as an anæsthetic by surgeons.\* As d'Arsonval states with infinite reason, the double-wall recipients with internal vacuum have been realised both as to form and use ever since 1887. If the description, strictly speaking, is reasonable in England, it is distressing in France to constantly hear these recipients called Dewar's cups.

The illustrious English scientist certainly devised, as far back as 1874, a calorimeter to which he applied the insulating properties of a vacuum to avoid the causes of error arising from the penetration of heat. But what shows the two objectives to have been very different, is that when manipulating liquefied gases at the laboratory of the Royal Institution during a series of memorable investigations continued ever since 1883, although exposed to continual difficulties through their rapid evaporation; though Dewar was the first to think of using suchlike recipients for liquefied gases, he did not actually do so

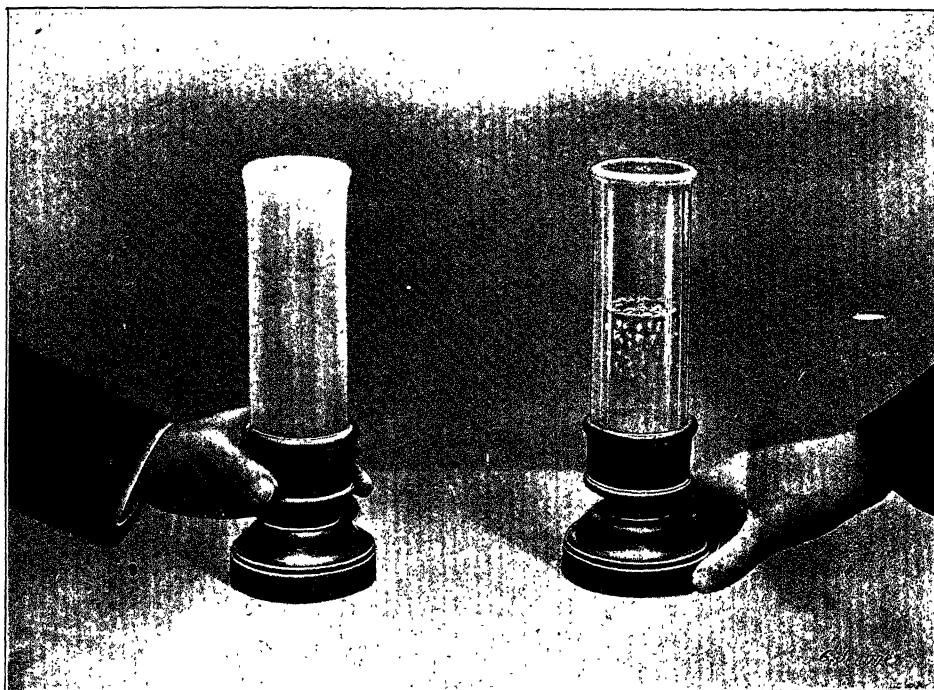
1892, that is, not till nine years after the very complete description given of them by d'Arsonval.

Notwithstanding everything, the recipients thus manufactured are still very far from being sufficiently efficient, difficult is the preservation of this extraordinary liquid. Evaporation is only reduced thereby, in the litre size of recipient, to about *one tenth* of what it was in the recipient

\* 'Proceedings of the Biological Society of France,' February 11th, 1888.

which was not protected at all—and this is far too little. Here (Figs. 68 and 69) is a beaker of this kind which is filled with liquid air.

After the agitation at starting has calmed down, you will see numerous bubbles continually rising in the liquid and rapidly increasing in size, which are nothing more than



FIGS. 68 and 69.—Insufficiency of the vacuum alone as a means of protection against heat. The liquid boils briskly, and after an instant the cup becomes cloudy and covered with rime.

bubbles of vaporised liquid air exactly analogous to the bubbles of water-vapour when boiling. Wait a minute and you will see the external walls of the recipient get covered with mist, and then, especially if the temperature is low, with beautiful arborescent figures similar to those which winter produces on the windows of our apartments,

#### 14 PRESERVATION AND PROPERTIES OF LIQUID AIR

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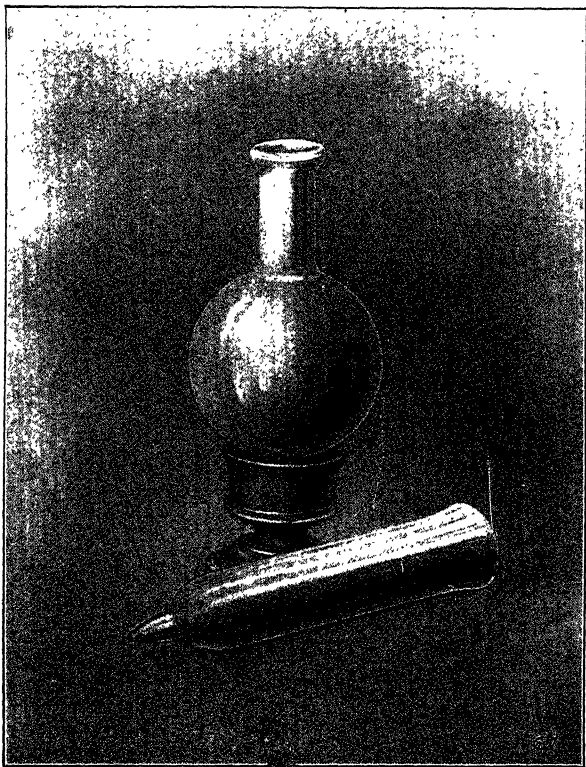
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is not very easy to successfully blow one within the other two concentric bottles, often of the capacity of several litres, whose walls are only a few millimetres apart.

This achievement, we, however, have to regretfully add, must cross the Rhine or the Channel to reach its address.



figs. 70 and 71.—d'Arsonval's and Dewar's silvered recipients with intermediary vacuum.

France it is practically impossible to have these recipients made. French specialists in this line have found it more simple to have nothing to do with the question, holding, no doubt, that they will be able to catch up the lost time, when the game is worth the candle. Such an argument is far too often used in France and elsewhere, while little by

little the foreigner in many an important issue, like the persevering tortoise, acquires such a lead that at the decisive moment it passes the winning post fifty lengths ahead of the sleepy hare.

The solidity of the wonderful apparatus thus manufactured, from certain points of view at least, is disconcerting enough to upset our ideas on the resistance of materials. If the external envelope is thick enough to resist accidental blows fairly well, the interior lining is of the thinnest possible glass, only *three tenths of a millimetre* in certain parts. Now this onion skin, this soap bubble, on account of the internal vacuum, has to support the whole of the atmospheric pressure, or 10,330 kgs. per square metre, which corresponds to about 1500 kgs. for a recipient of 5 litres !

The result is all the more extraordinary that this internal lining and the external envelope are united, as Fig. 70 shows, along their lips, about 6 cm. in length—united by a weld as fragile as are all welds of glass.

Well, when the recipient is full of liquid air, not only does the lining bulb resist without giving way to the pressure of the 1500 kgs. mentioned above, but we can transfer the liquid and empty the recipient by inclining it. The weld is exposed in that case at the end of the long arm of a lever to a transverse strain due to the considerable weight of the fragile internal bulb with its 5 litres of liquid air ! We can very rightly marvel, it would seem, at such a result.

We should not, however, conclude therefrom, that except in the case of simple beakers of small volume, this practice of transferring the liquid air by inclining the recipients which hold it, is to be recommended.

Very far from it !

The misfortune, moreover, is that these recipients, so extraordinarily resisting in certain ways, behave, nevertheless, in a deplorably capricious fashion under the influence of the cold of liquid air, especially when the latter comes in

contact with the weld which unites the lips of the two balloons at the top. Nine times out of ten nothing occurs, and we can transfer the liquid air without any precautions from one recipient to another without anything untoward happening; the tenth time, when the first drop of liquid air reaches the badly conditioned weld—crack! A slight noise, an ill-omened rending sound, followed by the covering of the whole of the outside of the bottle with rime, tells you that the latter is only fit to be cast on the scrap-heap—and thirty or forty francs to be written down on the wrong side of the profit and loss account. And here, at least, is an operation with which those who manipulate liquid air will not be long in becoming familiar.

On other occasions things occur in a more lively fashion. The rupture is accompanied by an explosion similar to that of an incandescent bulb, and caused, as in that case, by the sudden entry of the external air into the intermediate vacuum, and likewise accompanied by the reduction to powder of the *inner* bulb, but generally without any danger to the operator.

This extreme fragility is all the more regrettable as these recipients, owing to the difficulty and the minute care required for their manufacture, are, as we have stated, costly. It makes quite a risky operation of all storage and transport of liquid air, and it is entirely due to this that the sale price of this liquid, which is so easy to produce at the present time, cannot fall below five to six francs a litre.

**Apparatus for withdrawals; precautions to be taken during the manipulation of liquid air.**—We cannot, therefore, take too many precautions in the manipulation of liquid air with the recipients we have been describing, the most essential being that the liquid air should never come in contact with the weld.

We use for this purpose a rubber cork with two holes,

through which are passed, first a plunging tube *a* (Fig. 72) with two bends, second, a short tube (*b*), ending in a rubber ball with valve (*P*), similar to that which hairdressers use for spraying their customers with questionable scents. The tube *a* is introduced into the recipient and plunged with care, because of the violent ebullition which the glass occasions on cooling by contact with the liquid air; finally, the bottle is closed by the cork. A certain quantity of

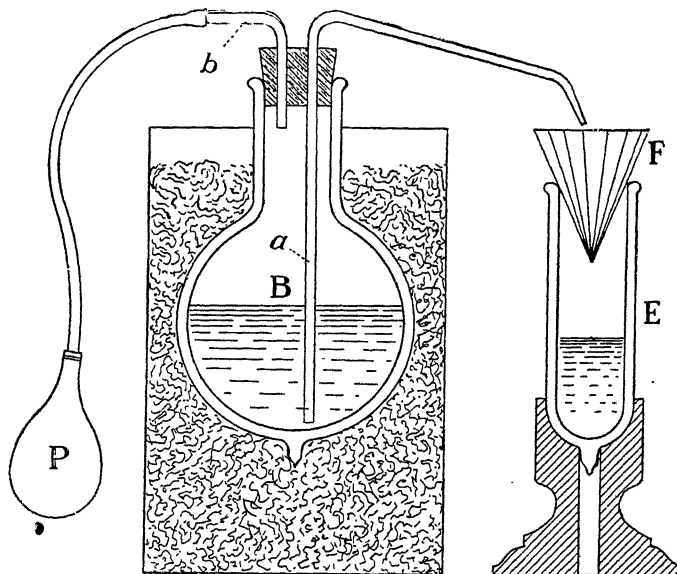


FIG. 72.—Liquid air flask with withdrawal attachments.

liquid air, especially if we have been rather quick, issues spontaneously through *b*, owing to the completion of the cooling of *a*. This is collected in the test-cup with double envelope, with which experiments are made, always carefully avoiding, for fear of breakage, any contact of the liquid air with the weld which forms the upper edge of the bottle. If the quantity issued of itself be not sufficient, we can add to it by squeezing the ball repeatedly.

The liquid air having been withdrawn, it is best to take out the cork, which, without this precaution, would freeze

and lose its tightness. It should be thus taken away after each withdrawal. Among other precautions it is best also not to attempt, for reasons of economy, to thrust the tube *a* through the cork too far, with the object of recovering the last drops of the liquid; for if this tube should strike the bottom when the cork is pressed home the bottle would inevitably explode. To avoid such an accident, it is well, above all things, to determine the depth of the bottle with a wooden rod thrust with due precautions down to the bottom, and to regulate with this the length of *a* below the cork, to suit; taking into account the amount the latter is thrust home into the neck, the end of the tube should reach within 1 or 2 centimetres of the bottom. The corresponding loss of liquid is insignificant. We can at the same time determine the quantity of liquid air at our disposal: it is sufficient when the rod touches the bottom of the bottle to wait an instant for it to be cooled; it is then taken out and it is waved for an instant in the air, and it gets covered with rime on the part which was immersed, which can be seen all the better if the rod be painted black. We can just as easily determine the level of the liquid air in a recipient by progressively plunging therein a piece of indiarubber-tube, the other extremity being held to the ear. The sizzling noise of a red-hot iron plunged in water, is produced the moment the tube touches the liquid.

The recipient from which we withdraw the liquid air is manifestly for the first few instants the seat of violent ebullition as well as all the various bodies or apparatus into which we plunge it for our experiments. This initial cooling in one and the other case must be conducted with prudence, and taking time, so as to avoid upsetting the recipient.

Transference directly of liquid air from one double walled recipient to another should also be avoided. We may succeed ten times, but will break everything the eleventh time.

If, however, circumstances oblige, we should proceed by small instalments, always turning the test bottle from which we pour through a certain angle, so that, thanks to the *heating*, of which we shall speak shortly, there should not be at any moment, real contact between the glass of the weld and the liquid air.

It is also well in this case to remove the ice which covers with a hard crust the neck of the recipients in which the liquid air has been kept for several days. We should remark that all these precautions, being taken and others also, the manipulator is always at the mercy of an accident of this kind, which is particularly disagreeable in the case of a lecture; the mischance is then a capital one, and it is necessary so as to be in a position to repair same, first, to keep in reserve some appropriate remark, which should not fail to put critics in a good humour; secondly, to always provide yourself with two bottles of liquid air, two bottles containing, say, 1 litre each, so as not to find yourself at the end of your tether in the eventuality, always possible, of an accident. The author gives this advice because of sad experiences.

Why should not these recipients be made of metal? you will say.

Verily, an undoubted progress will be realised the day when we shall be able to reach such a result. The problem is, unfortunately, not one of the easiest, but it is not insoluble. We have already reached in this direction some hopeful results, of which we shall speak further on (p. 268).

**Efficiency of the d'Arsonval and Dewar recipients.**—We have not spared our criticisms, as compensation for some dozens of experiments which failed and no end of lectures which were compromised thereby.

Now let us pass to compliments.

Fragility apart, the results obtained by this very rational combination so elegantly developed in the form of d'Arsonval's and Dewar's recipients are simply marvellous.

Filled with a liquid whose temperature differs from the normal temperature by over *two hundred degrees*, their external surface allows nothing of this to appear, and is not even covered by the slightest mistiness. We can well understand that under these conditions the duration of the preservation of liquid air may become very long. A balloon of 5 litres' capacity belonging to d'Arsonval still held a little liquid air twenty-eight days after it was filled. Twenty-eight days in a balloon is a record which aeronauts after a century and a half of efforts have only beaten in the pages of Jules Verne, and we have the right, comparatively speaking, to congratulate ourselves hugely.

It should be remarked, however, that all these recipients do not behave in such a brilliant fashion as the peerless one just mentioned. It is necessary, in fact, that the vacuum should be pushed to its extreme limit (equal to Crooks' vacuum). The last molecules of the air play a capital part in actively transporting heat from one wall to the other without being affected thereby in their evolutions, as is the case with less perfect vacua, owing to their collisions with each other. Moreover, we can obtain recipients capable of preserving liquid air for from eight to fifteen days pretty currently—it being understood that with liquid air, *preserving* for eight days means that at the end of the eighth day the last drop has disappeared.\* This implies that the calorific transmissibility, which was already reduced to one tenth by the vacuum, undergoes a still greater reduction by the silvering, whereby the total reduction reaches to one two hundredth. These recipients call for a further interesting remark. If they prevent the access of heat to their interior when holding a hot liquid, they will also prevent with equal efficiency this liquid from getting cold. For instance, coffee which was boiled ten days ago, before being placed in such a recipient, could still be drunk now without risk of burning the throat.



It should be remarked that contrary to what would be done with liquid air, the recipient has to be corked to prevent the escape of the internal steam, which in this case is lighter than air. It is on this principle that *thermos* flasks are made, whose use is rapidly spreading, and which,

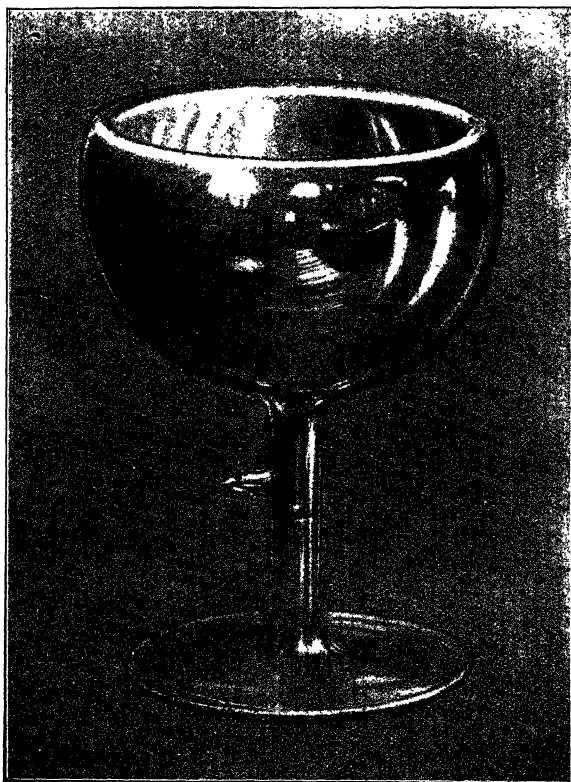


FIG. 73.—Liquid air cup.

in accordance with the season, preserve the cold or hot drinks which are placed therein.

Besides the bottles with double walls, which are more specially designed as holders for liquid air, Fig. 73 shows another form of recipient—a test cup with foot, like a champagne glass, which is used in the many very curious

xperiments to which liquid air lends itself, which is also made on the same principle of intermediate vacuum with internal silvering.

In lecturing, however, it is often more convenient to use recipients with vacuum walls which are *not silvered*, which allow the audience to more easily follow the experiments. In these experiments of short duration the slightly more rapid evaporation does not signify, because two or three litres of liquid air suffice to illustrate the lecture of the most prolix lecturer.

**Use of low temperatures for the production of perfect vacua.**—We have just seen how extremely important, from the technical point of view, the securing of perfect vacua to the preservation of low temperatures—for vacua which extend to one ten thousandth of an atmosphere, for example, would be wholly insufficient to produce good recipients for liquid air.

Now it is very curious to observe that the low temperatures themselves furnish precisely the most efficacious and most convenient means which is known for obtaining these extraordinary vacua: the whole question is to have at our disposal some *liquid hydrogen* and to follow the instructions of Sir James Dewar, which amounts to saying that the process for the present is not within the means of everyone. Liquid hydrogen, which is a substance ever so much more extraordinary than liquid air, since it only weighs 7 grm. per litre and boils at  $-252^{\circ}\text{C.}$ , is as yet not produced, as far as the world is concerned, save in certain exceptional laboratories besides that of Professor Dewar at the *Royal Institution*.

However this may be, this is the process, and we shall see that it is worth mentioning.

The recipient in which we wish to produce the vacuum, be it a Crooks' tube, a balloon flask, a recipient with double walls or what not, is united by a glass tube soldered to a

small bulb, also of glass; this is plunged for a few instants in a recipient containing liquid hydrogen. At this extraordinary temperature of  $-252^{\circ}\text{C}$ . the air is not only liquefied, but congealed to the extent of no longer possessing the least vapour tension: thus all the molecules of air in the flask, down to the last, precipitate themselves in a flash into the bulb and there solidify. A puff of the blow-pipe separates the bulb from the recipient and the trick is done; the vacuum thus produced in a few seconds is so perfect that the electric spark cannot traverse it.

It is useless to remark that under those conditions there is no necessity to take the trouble to make a vacuum beforehand in the double-walled recipients required to hold the liquid hydrogen, as this liquid must automatically surround itself, as with a halo, with a vacuum to which there is no parallel.

But liquid hydrogen is also, as we have just stated, a very rare product, very difficult to obtain, and we cannot dream of superseding by its aid the difficult and lengthy means which have been used up to this time in the manufacture of incandescent electric lamps, the bulbs for radiography, the recipients for liquid air, etc.

We could, it is true, get round the difficulty by filling the recipients to be exhausted with carbonic acid, then exhaust them as far as possible with an air-pump, then condense the residuum by means of liquid air. At the best the results would be very far from equally good, because of the traces of air which the carbonic acid always contains, and of the extreme importance, which we have recognised as belonging to the last traces of gaseous matter, and which are inevitably present under these conditions.

Happily, as we shall presently see (p. 263), thanks to another very important discovery of Dewar's, an infinitely preferable method may be substituted:-

**Impossibility of preserving liquid air in closed vessels.**

—If liquid air can be easily preserved in the *open* vessels of which we have been speaking, it would be wrong to think that it could be preserved better still in *closed* metallic recipients, which would entirely prevent evaporation. Many have been those who have fallen into this error!

However paradoxical it may seem, it is absolutely impossible to preserve a *single drop* of liquid air in a closed recipient, though it be supposed to be sufficiently solidly made to resist the enormous pressures which would be brought into play.

Moreover, in an open recipient the penetration of heat compensated for at each instant, by the cold resulting from the evaporation of a corresponding quantity of liquid, and the remaining liquid is able to maintain in this way, until complete evaporation, its temperature of  $-190^{\circ}$  C. In a closed recipient, on the contrary, this cannot be the case. Here the penetrating heat, instead of being constantly eliminated outside with the products of evaporation, will necessarily be accumulated in proportion as it penetrates into the recipient, whence a parallel and progressive rise in the temperature and in the pressure of the liquid air, which will rapidly attain to its critical temperature of  $140^{\circ}$  C.

But above this temperature we know that the air cannot any longer remain in the liquid state; it will, therefore, take on the gaseous state as a whole, and develop naturally a most formidable pressure, which might eventually attain 800 atmospheres, since the density of liquid air is 800 times that of gaseous air at the ordinary temperature. The recipient would thereupon be transformed into a formidable shell, but it will no longer hold a single drop of liquid air.

Here, in corroboration of the preceding explanations, is

a small experiment which is not devoid of interest. In a welded iron tube, closed at one end (Fig. 74), a small amount of liquid air is poured, and when the violent ebul-

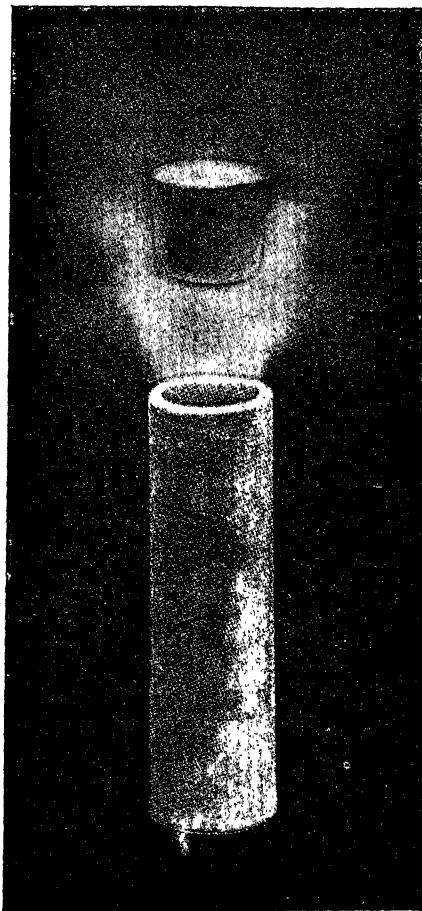


FIG. 74.—Violent expansion of liquid air evaporating in a closed vessel.

lition at first started is calmed, the tube is closed with an india-rubber cork. At the end of an instant the rapid increase of pressure in the interior of the tube suddenly brings about the violent ejection of the cork.

An English company uses this process to manufacture

metal cartridges, which, being hermetically closed, explode when the internal pressure has increased sufficiently. This company asserts that very favourable results can thus be obtained in working certain coal and other mines where ordinary explosives producing flames, even those which we are learning to make with coal and liquid air, could not be used without danger.

We can gather from the above explanations that the only gases capable of being preserved in the liquid state in steel bottles are those whose critical temperature is higher than that of the environment, that is, those which can be liquefied by the effect of pressure alone, such as carbonic acid, sulphurous acid, etc. All others, *e.g.* oxygen, hydrogen, nitrogen, etc., can only be stored in the gaseous state.

## CHAPTER IX

### PROPERTIES AND PHYSICAL EFFECTS OF LIQUID AIR

**Colour.**—Why is the sky blue? What notes of discord has this question not sown in the physicists' camp? Now, as you can perceive from this sample contained in a non-silvered holder, liquid air possesses an unmistakably blue colour, due to the oxygen it contains, which is all the more intense the more oxygen is present. This blue colour recalls exactly the colour of the sky.

Almost always the appearance of liquid air is opalescent and off colour, and the opalescence is often accentuated so as to give the liquid a milky appearance. This appearance is more noticeable when the liquid air issues from the manufacturing apparatus, and when the drying and decarbonisation of the air have not been carried very far, and is due to the presence of diminutive crystals of carbonic acid and of water produced at this unusual temperature. It is easy to relieve the liquid air of these impurities by filtering, which can not only be effected by using an ordinary filter—a result always received with surprise by the numerous people who are inclined to deny to such a liquid the properties of ordinary liquids—but which can be carried out, as you will observe (Fig. 75), with extreme ease. Those who see the experiment for the first time, especially chemists, to whom difficult filtrations are one of the plagues of their lives, never give up believing that the filter has a hole through it; nothing of the kind is the case, because you can see that the liquid is perfectly limpid and mobile, and that the impurities remain on the filter as a crystalline down.

## 10 PRESERVATION AND PROPERTIES OF LIQUID AIR

The filter should be placed in a metallic tundish or can, used alone as shown in the figure. A glass tundish could probably suffer badly from the operation, and its leaking would bring about sympathetically the breakage of the test-glass.

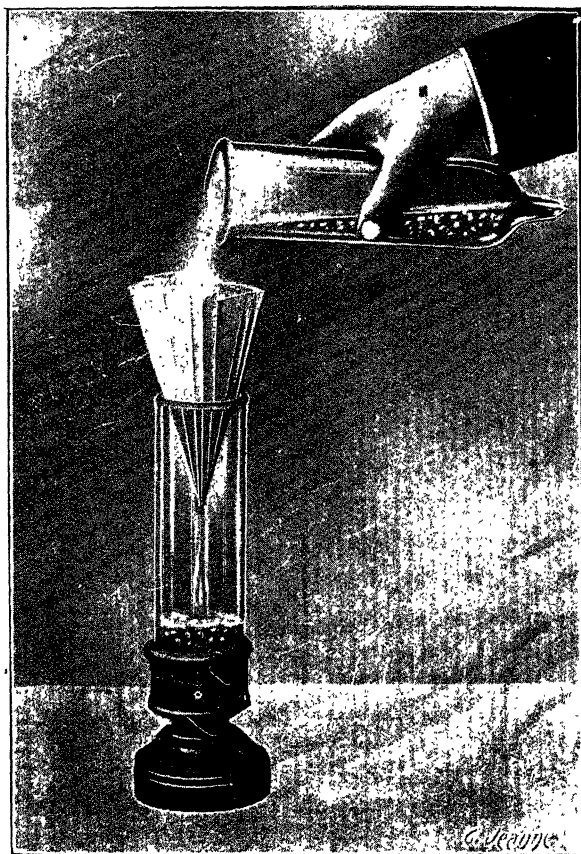


FIG. 75.—Filtering liquid air.

**Variation of the boiling-point of oxygen mixtures with their composition.**—So far as concerns the temperature of boiling of liquid air under atmospheric pressure, we have several times given the figure as  $-193.5^{\circ}\text{C}$ . Now this figure refers to liquid air of normal composition,



that is, containing 21 per cent. of oxygen. In point of

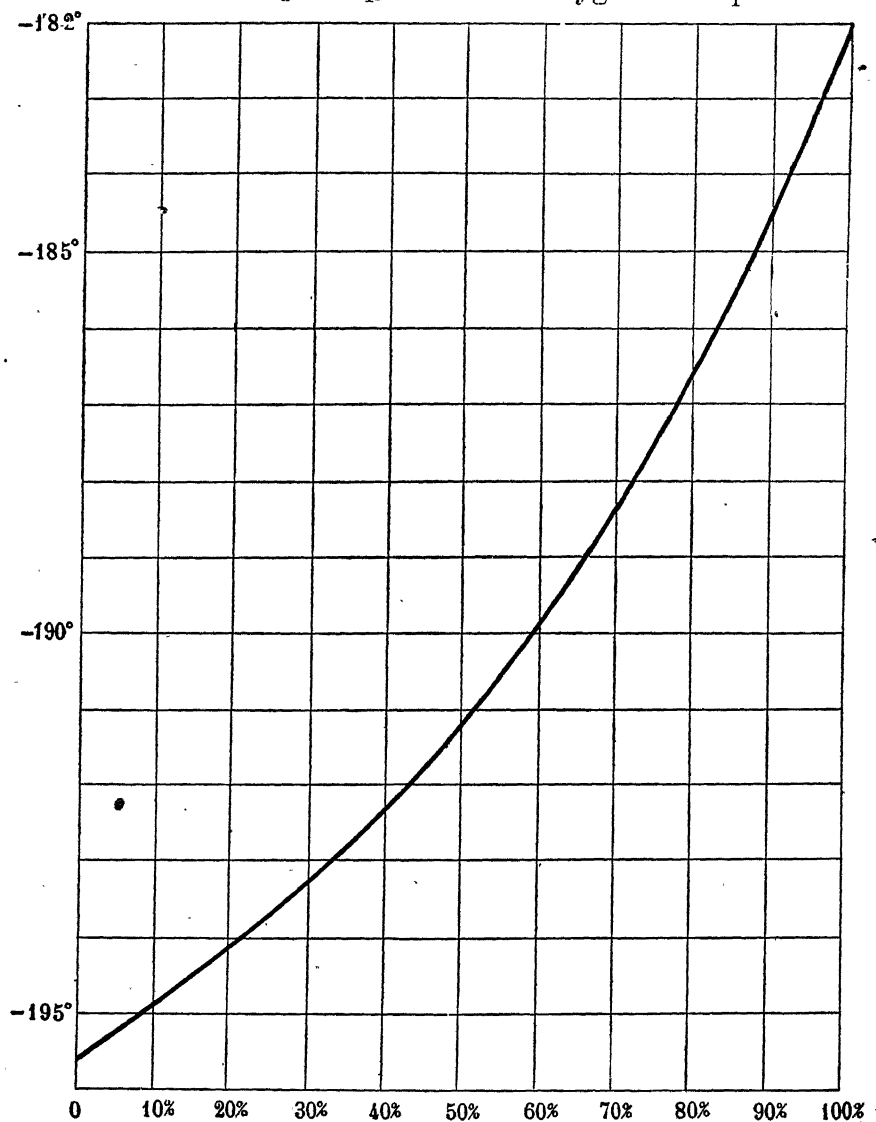


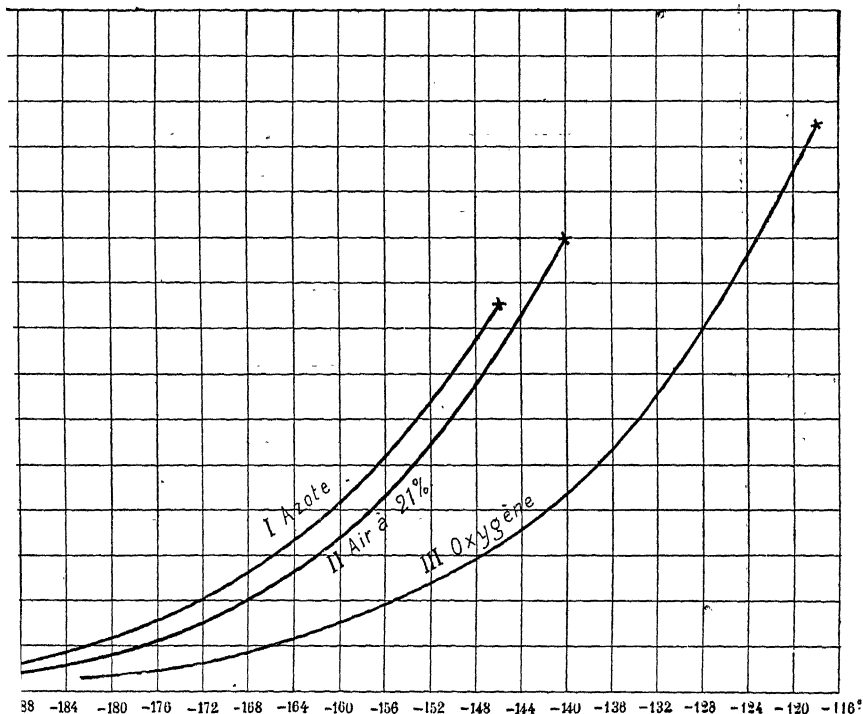
FIG. 76.—Variation in the boiling-points of the mixtures of oxygen and nitrogen according to their composition taken as abscissæ.

fact, liquid air of this composition is hardly ever met with in practice, for we shall mention further on the extremely

## 2 PRESERVATION AND PROPERTIES OF LIQUID AIR

important fact that when liquid air evaporates, its two components participate unequally in this evaporation, so that the liquid is progressively enriched in oxygen, and attains at the end of evaporation, a composition approximately very pure oxygen.

*Pari passu* with the development of evaporation, the



77.—Vapour tensions of normal liquid air, of nitrogen and of oxygen as functions of the temperature (or temperatures of ebullition under pressure).

perature of boiling is raised, and having started from  $-193.5^{\circ}\text{C}.$ , it finishes up finally and inevitably at the perature of ebullition of pure oxygen, viz.  $-182.5^{\circ}\text{C}.$  We have drawn in Fig. 76, according to Baly's experiments described further on, the temperature of mixtures liquid nitrogen and oxygen, not only for the composition of normal liquid air, but for the composition where oxygen = 0. The temperature under these conditions

starts from the point of ebullition of liquid nitrogen. It will be remarked that the temperature of ebullition is rising more and more rapidly in proportion that higher compositions are reached. This is due to the fact that up to a rather high composition oxygen only plays a very secondary part in the evaporation, as Baly's curves will show (p. 305).

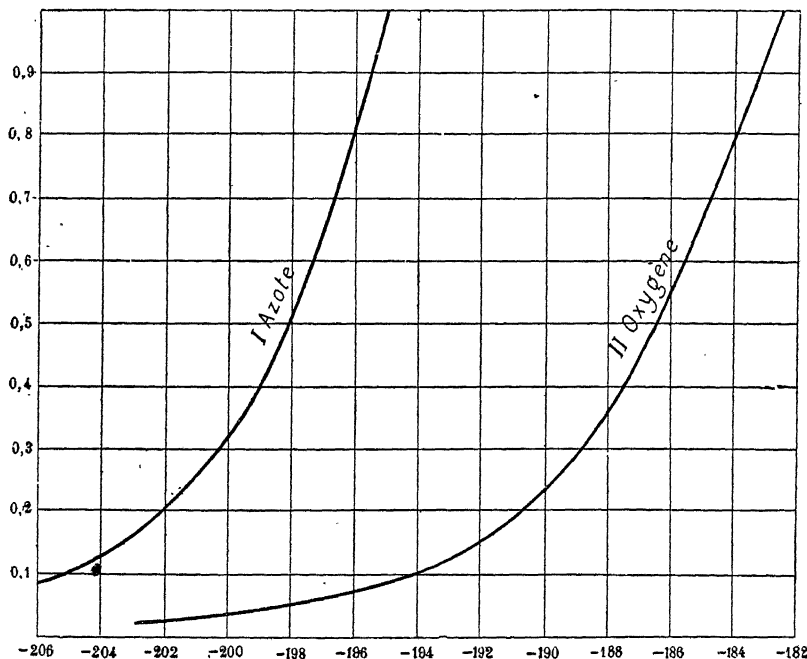


FIG. 78.—Vapour tensions of oxygen and nitrogen at very low temperatures (or the temperatures of ebullition under reduced pressure).

**Variation of the boiling-point or of the point of liquefaction with the pressure.**—Curve No. II, Fig. 77, shows how the pressure influences the temperature produced by the ebullition of the air or its converse liquefaction. This curve only gives approximate results, because we shall see that the liquefaction of air, like its evaporation, implies the phenomenon of the separation of its two elements, so that for the same temperature the pressure

varies with the amount liquefied. Strictly speaking, what should be drawn is, according to Duhem's nomenclature (p. 350), a curve of the *dew points* of the air at different pressures and a curve of the *points of ebullition*. The necessary determinations however have not, as far as we know, been yet made.

Curves I and II of the same figure represent respectively the vapour tensions of the oxygen and nitrogen as functions of the temperature.

Curves I and II (Fig. 78) have the same meaning as the preceding, but for pressures lower than atmospheric pressure. We see how considerable is the variation in temperature due to this simple variation of 1 atmosphere below atmospheric pressure, and how efficient, therefore, is the use of a vacuum to lower the temperature of these liquids. This is due to the variation in temperature depending in a great measure upon the *ratio* of the initial pressure to the final pressure, a ratio which is usually large, for example, between 1 atmosphere and 0.1 between 10 atmospheres and 1.

We can, moreover, easily understand that it should be so, because, according to the explanations we have given (p. 10), the temperature of a liquid, in presence of its own vapour alone, is fixed at the point where the vapour tension balances the pressure.

Now it is theoretically only at absolute zero that the vapour tension of a liquid = 0, so that if the pressure supported by the liquid could be reduced down to 0—that is to say, if its vapour could be completely absorbed so as to maintain an absolute vacuum—the temperature of this liquid would fall of itself to absolute zero.

**Densities of liquid air, of liquid oxygen and of liquid nitrogen.**—Let us pour into a glass filled with water a small quantity of liquid air (Fig. 79). The violent ebullition which is evolved is accompanied by thick velvety smoke pro-

ducing the most beautiful effects, especially in a brilliantly lighted room. We can see the liquid globules forming, which, though at first confined to the surface, dip afterwards deeper and deeper into the water notwithstanding the violent ebullition. This is due to the density of liquid air,

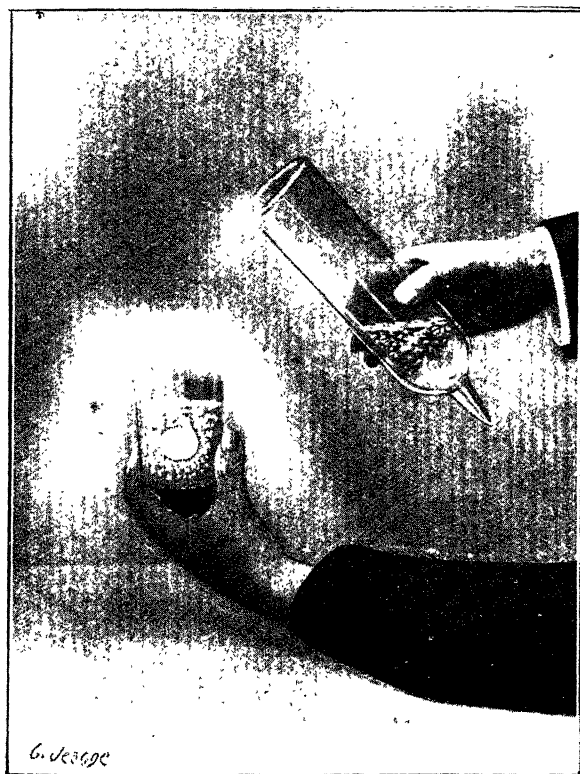


FIG. 79.—Experiment on the density of liquid air.

by a curious coincidence, being approximately equal to that of water, a little more or a little less according to its contents of oxygen.

At the first starting of evaporation, the liquid, being lighter, remains therefore at the surface of the water, but becoming more and more dense as the evaporation continues, the

curious dipping we have noticed is brought about. Exactly the density of liquid nitrogen under atmospheric pressure = 0.880 of that of water, while that of oxygen = 1.120.\* The two liquids mix without sensible contraction, so that, as d'Arsonval has remarked, a knowledge of their density obtained by using a simple density-meter results at once in knowing their composition. For if  $x$  and  $(100 - x)$  be the respective compositions in oxygen and nitrogen and  $A$  the density observed, we have—

$$\frac{x \times 1.120 + (100-x) \times 0.880}{100} = A;$$

hence—

$$x = \frac{100A - 88}{0.24} \text{ and } (100-x) = \frac{112 - 100A}{0.24}.$$

**Heat of evaporation of liquid air; its use as a refrigerant.**—The time has now come to destroy a legend.

It will have been remarked that in the preceding experiment, notwithstanding contact with such an extremely cold liquid the water in the glass remained perfectly liquid. Now certain writers, who have never seen a drop of liquid air and are all the more anxious to appear well informed, state barefacedly that the said drop suffices to freeze a glass of water entirely, and that the kingdom of ice is at an end.

This is wholly untrue as we have seen.

In point of fact the liquid in the glass is much cooled, but at most a very slight film of ice will be floating on the surface at the spot where each globule of liquid air has completed evaporation.

Effectively, so far as *quantity* the cold stored by liquid air is nothing extraordinary; far from it; its heat of evaporation is very closely 50 calories per kilogramme,† so that—expected fact—we find that 1 kg. of liquid air when

\* Olszewski, 'Wied. Annal,' 1886, xxxi, p. 58.

† Oxygen 51 calories per kilogramme, nitrogen 48 calories per kilogramme.

evaporated produces *notably less cold* than 1 kg. of ice when melting, which absorbs, in fact, in this fusion 79 calories! It is true that by arranging matters suitably we could add the heat of *heating* up the gas evolved, to the heat of evaporation, which would bring up the total refrigerating effect of 1 kg. of liquid air to that of 1.25 kg. of ice; it is assuredly not much, and we might have expected better, but it is what it is, which suffices for those who know.\*

Thus it follows that what is remarkable in liquid air is not at all the quantity of cold which it brings into play, but the *quality* of this cold, the extraordinary low temperatures which are attained thereby; it is because of this very quality, that the cold stored in liquid air is obtained at very much greater expense than that involved in ice.† Whence this conclusion. If this quality of cold is necessary for the frigorific application we have in view, if we wish by its help to freeze alcohol, for example, the employment of liquid air will be quite logical, and perfectly justified, but its use would be ridiculous if the *quality* of the degrees of cold was a matter of indifference, as is the case when it is the question of icing bottles or of holding back the fermentation of beer. To use liquid air instead of ice under such circumstances would be just as unreasonable as to pump water from a depth of 190 metres when we had at our disposal a well of ten metres depth or water from a spring.

Also, generally, the uses to which ice is actually put would not at all justify, as has been contended, the use of liquid air. This would be an unreasonable application which people have a mania for proposing, and which it is most assuredly the interest of the new industry to decline.

Be it understood, we must exclude from this severe

\* We can still further increase the frigorific effect of liquid air by about a dozen calories by making the air evaporated under pressure perform some mechanical work.

† A horse-power hour, as we have seen, produces in practice 100 degrees of cold in the form of liquid air; it could furnish more than 2000 in the form of ice.

criticism the cases where some effect which is peculiar to liquid air besides refrigeration comes into play. For instance, liquid air might be usefully employed when it is desired to obtain cold which is absolutely devoid of moisture as is the case often in the question of conserving food, in the wine-producing industries, etc., and better still in the



FIG. 80. — Liquid air poured with impunity on the back of the hand.

renewal of air, where its superoxygenation is a matter of moment, which might be the case when the management of a theatre were anxious to secure for their building a good reputation in sanitary circles.

**Specific heat of liquid air.**—According to Dewar's researches the specific heat of liquid air is about half that of water, viz. 0.5.



**Singular effects due to calefaction.**—On account of its excessive temperature, we might fear that liquid air might be a terribly dangerous body to handle. Now, here is a surprise. We can let a stream of liquid air fall on the back of one's hand (Fig. 80). Nothing happens. We can plunge a finger into liquid air. Again nothing happens.



FIG. 81.—How you can with impunity take liquid air in your mouth.

Still better : The operator who was photographed for Fig. 81 turned into his mouth the stream of liquid particles produced by the sudden immersion of an india-rubber tube in a test-glass containing liquid air. He does not, it is true, look very happy over it, but this may be due to lack of enthusiasm. You must not, however, push

the experiment to the extent of swallowing a mouthful of this liquid air, as d'Arsonval's unfortunate victim did, who suddenly found himself swelling like an air-ball, and had promptly to deflate himself by the best means at his disposal.

What is the meaning of this extraordinary innocuousness of liquid air for our organs? It signifies simply

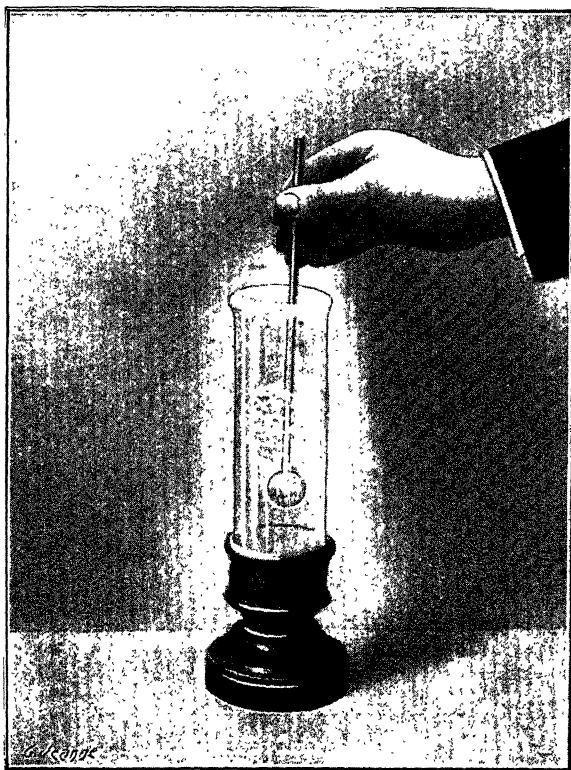


FIG. 82.—Experiments on calefaction.

that the interesting phenomenon of *calefaction* intervenes, wholly identical with that which is produced when a drop of water deposits itself on an iron plate which is red-hot: owing to the very high temperature of the skin in comparison with the liquid air, a layer of evaporated air is

formed between the liquid air and the skin, which prevents a contact, which, if it took place, would inevitably destroy the tissues after the fashion of a violent burn.

But, undoubtedly, we must beware, in these experiments, of an excess of confidence in the virtues of calefaction, and certainly not abandon one's finger too long to the liquid air. A few seconds longer would possibly allow you to escape with a very serious burn ; yet a few seconds more and your

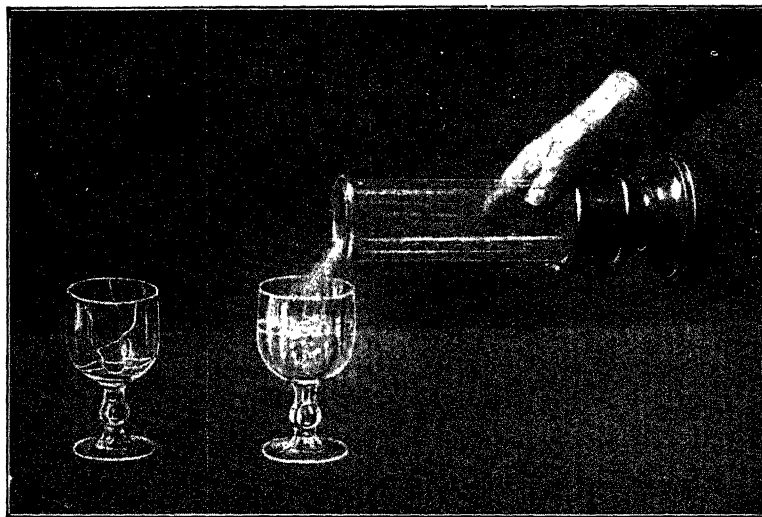


FIG. 83.—The order is to break—crack !

finger would be nothing more than a small motionless yellowish object, very easy to break with the blow of a hammer.

However unexpected the preceding experiments may appear, this remarkable property of calefaction can be made apparent in still more striking manner by the following experiment : A metallic ball of from 1.5 to 2 cm. diameter is immersed in liquid air in a transparent test-glass (Fig. 82). The ebullition is at first relatively moderate, and continues such during one or two minutes, because

the ball is not wetted, and the gaseous layer which very visibly surrounds it prevents its rapid cooling. At a given moment the ball is cold enough for the liquid to wet it, and an enormous renewal of ebullition is suddenly observed.

It is also by reason of an identical phenomenon that this thick glass, into which we are going to suddenly pour liquid air (Fig. 83), will not break at first starting, as the liquid air is not in intimate contact therewith. At a given moment, the glass, having progressively cooled, the liquid air can suddenly wet it, and most probably you will see it fly into splinters through its violent contraction at the points of contact. If, however, the glass contains a little water, we can, without risk, pour liquid air into it, as we have seen (Fig. 70). We can therefore with impunity, in old fashioned champagne glasses, *cool our champagne* with liquid air to the accompaniment of thick velvety smoke of the most attractive appearance.

Thanks to calefaction, direct contact with liquid air in case of breakage of recipients or other circumstances is, therefore, much less terrible than we might think, and it is even in general inoffensive, but to touch it with metallic articles cooled through contact therewith may be much more disagreeable, as there is no longer any gaseous layer which can intervene. Therefore it is well not to touch these objects save with the protection of a piece of waste, being careful that the waste has not imbibed liquid air, otherwise its contact would be very disagreeable—not to say dangerous.

**Liquid air is innocuous for microbes.**—Microbes can quite easily accommodate themselves to liquid air. To their profound astonishment bacteriologists have been compelled to acknowledge how feeble is the action of liquid air on the majority of these minute organisms. When a modest temperature of  $+ 60^{\circ}$  or  $80^{\circ}$  C. is enough to destroy them, the  $- 190^{\circ}$  C. of liquid air seems not to

affect many of them at all. The proof is that after three weeks' immersion, Charrin's pyrocyanic bacillus, when brought back to a less cold world, recommenced quite philosophically to secrete the blue matter from which it derives its name. Certain scientists have even introduced some obvious improvements in the above *modus operandi*; they have cooled down, then warmed up the microbes for a number of times, submerging them on each occasion in liquid air, then without any intermediate stage into water at  $+50^{\circ}\text{C}$ . Nothing happened to them! When brought back for the last time to the ordinary temperature they were at once ready to recommence their terrible career. D'Arsonval has given an ingenious explanation of this extraordinary immunity, based on the evident extraordinary character of the osmotic pressures in the microscopic bacterial cells. Under these enormous pressures the water in these cells could not possibly freeze even at  $-190^{\circ}\text{C}$ ., and the cells would thus escape from destruction, to which they otherwise would inevitably be condemned.

This, in any case, is a singular contribution to the seductive theory of the common origin of life in the universe, since it shows us that under the condition of a celestial catastrophe, vital germs could be transported from one world to another without being stopped by the enormous cold of interplanetary space.

**Magnetic properties of liquid air.**—Since we are studying the physical properties of liquid air we ought to point out one of a somewhat special order, but so remarkable that one cannot really pass it in silence. Liquid air, in fact, shares with iron, nickel and cobalt, the curious property of being *magnetic*. Assuredly its magnetism is not comparable with that of iron, but it permits it, however, as Dewar has shown, to attach itself to the poles of a powerful electro-magnet (Fig. 84) from which it detaches itself as soon as the current is cut off.

This property is due to the oxygen, in connection with which it was first pointed out about 1840, by Becquerel, who was operating with wood charcoal saturated with oxygen. It is, therefore, all the more marked and the more pronounced the more the liquid is oxygenated.

Moreover, when liquid air is placed between the poles, it is not only the oxygen but the whole of the liquid which remains suspended; there is no separative action. When, however, we cause the nitrogen of the air to *solidify*, which will be spoken of later, by boiling the liquid air *in vacuo*, the oxygen remains in liquid state in the frozen mass which

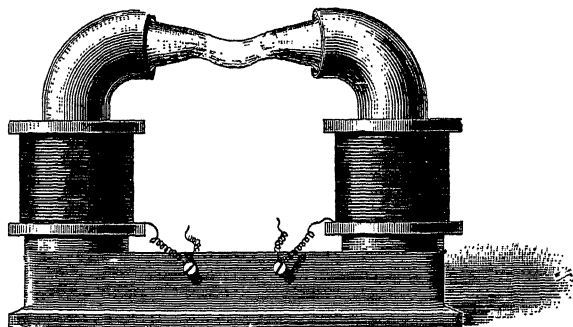


FIG. 84.—The magnetism of liquid oxygen.

is formed, and we can then by means of an electric magnet cause the drops of oxygen to issue from the meshes of the mass in which they are imprisoned.

We are therefore in the position, at the present moment, to separate out the molecules of the air with a magnet, exactly as we can separate out iron filings from copper filings.

It is an occasion, it appears, for affirming that science often reserves singular surprises for us!

We can carry out under another form, more visible to a numerous audience, the following experiment with the magnetic properties of oxygen. A test-tube of thin glass filled with liquid air is suspended from a long thread attached to a bracket. We approach the tube to an

electro-magnet, which we magnetise: the tube remains attached. We cut off the current: the tube falls.

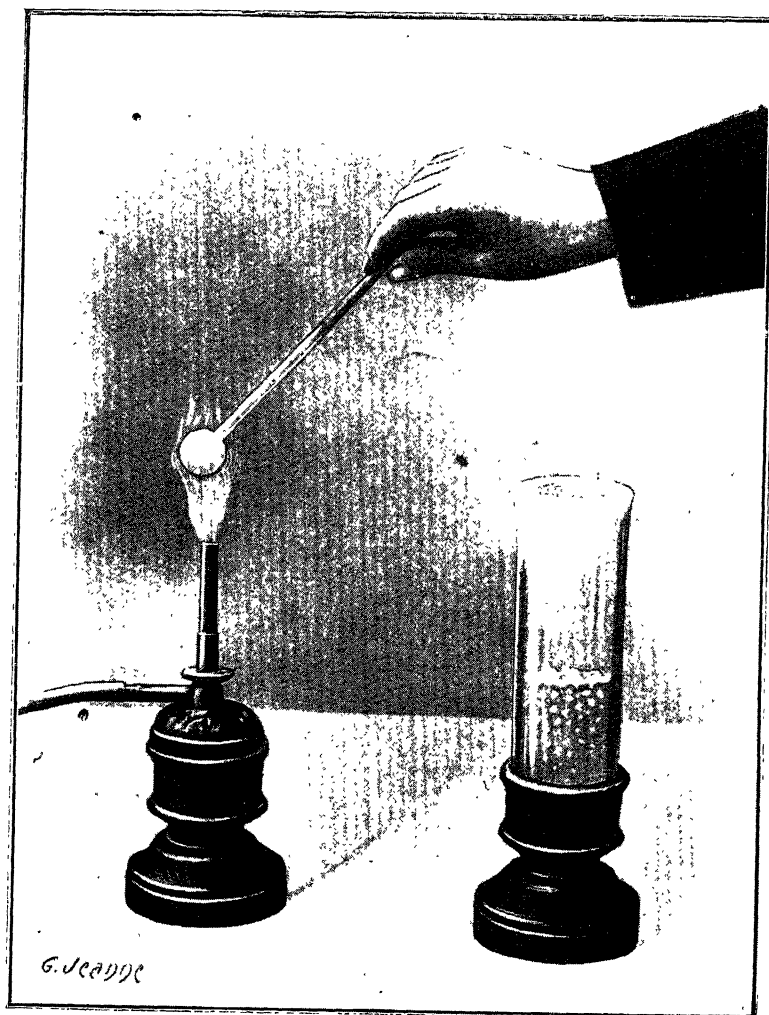


FIG. 85.—Production of snow in the flame of a gas-jet.

To succeed properly, we must have a powerful enough electro-magnet and a very long string, 1·5 to 2 metres in

length, so that the angle of the string with the vertical when the tube is attached may be slight.

**Consequences of the extreme cold of liquid air; production of snow in the flame of a Bunsen burner.**—A great proportion of the properties of liquid air are essentially due to its very low temperature. Nothing discloses this in appearance, but if we plunge into this calm and limpid liquid a mercury or alcohol thermometer, they are frozen up and

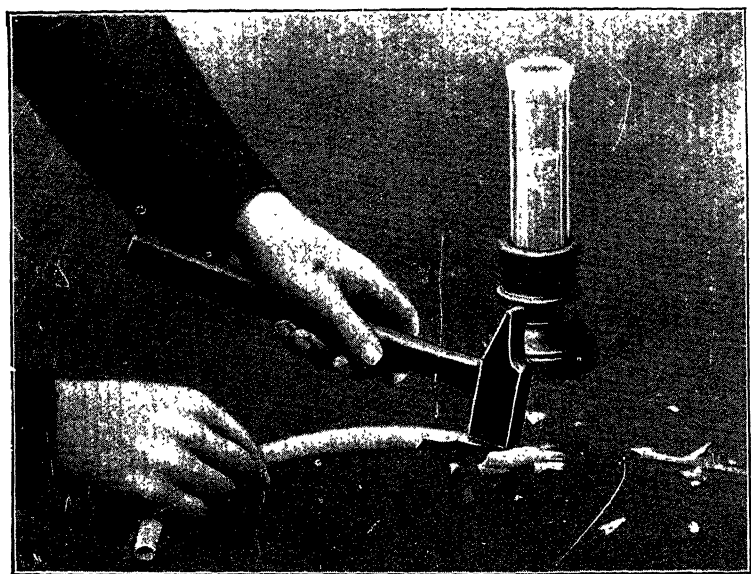


FIG. 86.—India-rubber tube coming out of the bath.

destroyed in the flash of an eye. The temperature of liquid air can, in fact, be only measured with electric thermometers (Fig. 28A), or by special thermometers of petrol vapour of which we shall speak presently.

It is difficult to show the extreme cold of liquid air in a more striking fashion than by the following experiment, in which the metallic ball which we used to demonstrate the phenomena of calefaction will again help.

Holding by its stem the refrigerated ball as above, let us bring it (Fig. 85) into the colourless flame of a Bunsen



burner. Strange fact! it gets covered, during a long moment, in this very hot flame with a layer of rime, becoming thicker and thicker through the condensation of the water and the carbonic acid of the flame.

**Hardening of various bodies in liquid air.**—We have risked, a short time ago, freezing a finger by plunging it in liquid air; this would only have been a particular case of one of the strangest properties of this substance—or rather of the temperature which it brings into play—that of hardening through contact, the majority of the bodies with which we are familiar, so as to make them unrecognisable. This india-rubber tube which we dip into liquid air becomes as stiff as a drum-stick (Fig. 86), and produces, when we strike it against a bottle, the sound of a metal rod, and breaks like glass under the hammer; these fruits, grapes, cherries, etc., all become veritable glass marbles, and rebound as such on a metal plate (Fig. 87).

The bills of fare of our meals would become very discouraging if we had to live at such temperatures. By the side of these fruits which have become as hard as pebbles, this beefsteak, warranted prime cut, breaks the plates quite gaily when taken from a short bath in liquid air. This is, indeed, one of the applications of liquid air which is most familiar to ordinary mortals. Happily there are on the credit side of its balance-sheet more ambitious achievements.

Nevertheless, all this is far from being only amusing, and could become the foundation of useful applications. Cork and meat, which are the despair of those who wish to reduce them to powder, can be thus reduced with the greatest ease when they have imbibed liquid air; wool and felt become very friable under similar conditions, and in this connection we would point out that a method of treating old hats as they deserve would be to dip them in liquid air and apply a stick to reduce them to fragments.

Another striking experiment, and which does not fail to

excite the liveliest interest at lectures, is the following: flowers, and, for example, this rose, are transformed in the liquid air into porcelain flowers, which at the slightest shake will fall into dust (Fig. 88).

Through an analogous effect, a pencil plunged into the liquid air, while it remains cold, loses its capacity for writing through the extreme hardening of the blacklead. This shows that we should be mistaken were we to think that the preparation of blacklead, which is used as a

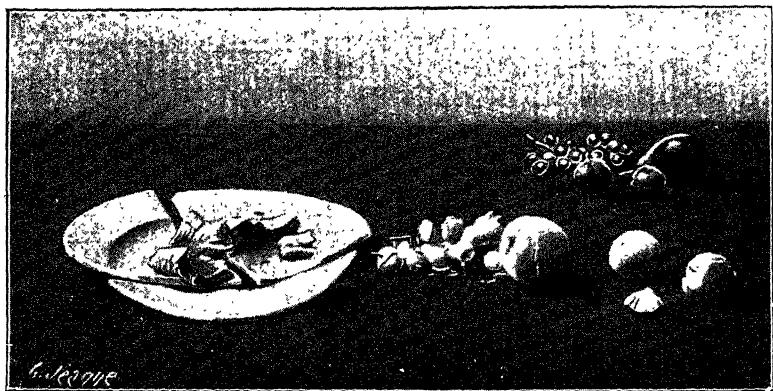


Fig. 87.—A beefsteak, armour clad; frozen and unfrozen fruit.

lubricant in many of the ordinary machines, could fulfil this use in liquid air machines instead of petrol ether.

All these effects are obviously physical and momentary, and the initial temperature being restored, the india-rubber, the fruit, the beefsteak, return, each in their own fashion, to their primitive condition.

**Modifications in the cohesion of metals.**—There is nothing, even metals, which does not find its cohesion in liquid air completely altered through the closer packing of its molecules.

Spiral springs of lead become competitors with those of steel when taken from liquid air, as you can see by the one (Fig. 89) which we have loaded, after being cooled, with a

rather considerable weight. Its temporary elasticity disappears almost instantaneously at the points where the operator's breath causes a current of warm air, which brings the metal back to its initial softness.

A leaden bell acquires in this refrigerating bath the sonorous qualities which we are not accustomed to find in this metal. Iron itself is profoundly modified in its properties to the extent that a sheet iron bottle filled with liquid air

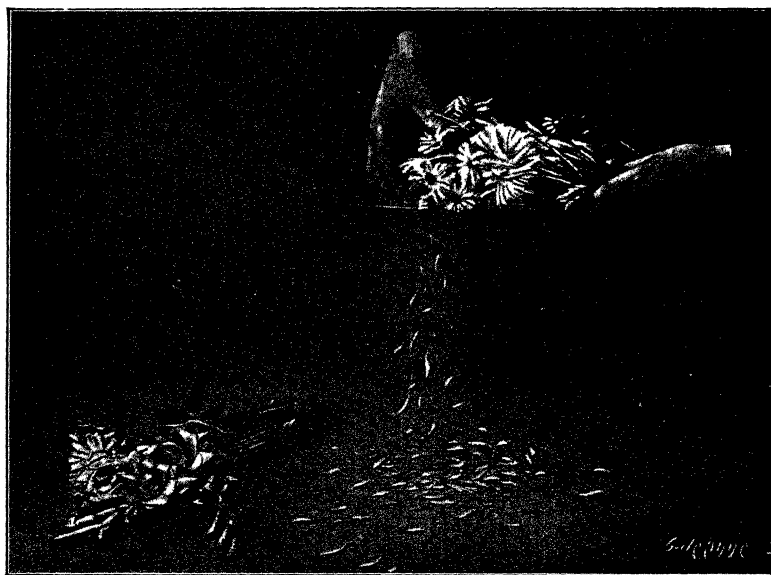


FIG. 88.—A bouquet refrigerated by liquid air.

becomes sufficiently friable to be broken with a blow of a hammer (Fig. 90). On the other hand, if the metal becomes friable its resistance to tension is enormously increased, to such an extent indeed that wire strands can support, without breaking, weights twice as heavy as at the ordinary temperature.

Here is an experiment in point which is wholly convincing: We have attached a 2 kg. weight to this handle by a lead wire, 1 mm. in section, which would be wholly

insufficient to support this weight, but this wire is passed through a small hole into a small glass sheath, which can be filled with liquid air by immersing it in a test-tube before hooking on the weight. The resistance to tension of this wire is then increased to such an extent that we



FIG. 89.—Paradoxical spiral spring.

can now raise the weight by the handle; only the heating of the wire is rapid, and after a few seconds it breaks (Figs. 91 and 92).

The following, according to Dewar, is the extent of the change in wires of various metals.

The data relate to the resistance to rupture of wires of 0.5 mm. diameter.

	+ 15°	- 182°
Soft steel . . . . .	190	317
Iron . . . . .	140	304
Copper . . . . .	90	136
Tin . . . . .	140	200
Gold . . . . .	115	153
Silver . . . . .	149	190

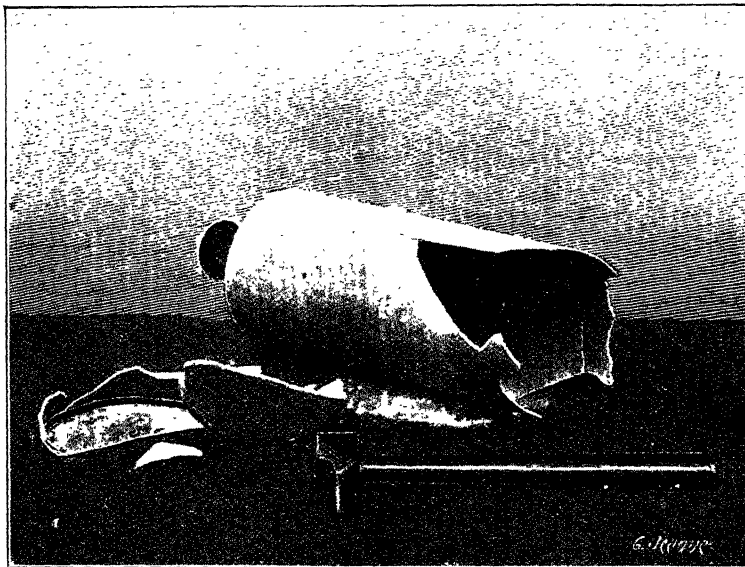


FIG. 90.—What a blow from a hammer does for an iron bottle after immersion in liquid air.

Lead itself more than doubles its resistance.

All these experiments are only amusing, but they open interesting vistas into the laws which govern matter.

#### FREEZING OF LIQUIDS: MERCURY, ALCOHOL, ETC.

As a matter of course, at these ultra-Siberian temperatures, almost all the liquids which we know take on the solid state. Mercury becomes frozen with an ease which

insufficient to support this weight, but this wire is passed through a small hole into a small glass sheath, which can be filled with liquid air by immersing it in a test-tube before hooking on the weight. The resistance to tension of this wire is then increased to such an extent that we

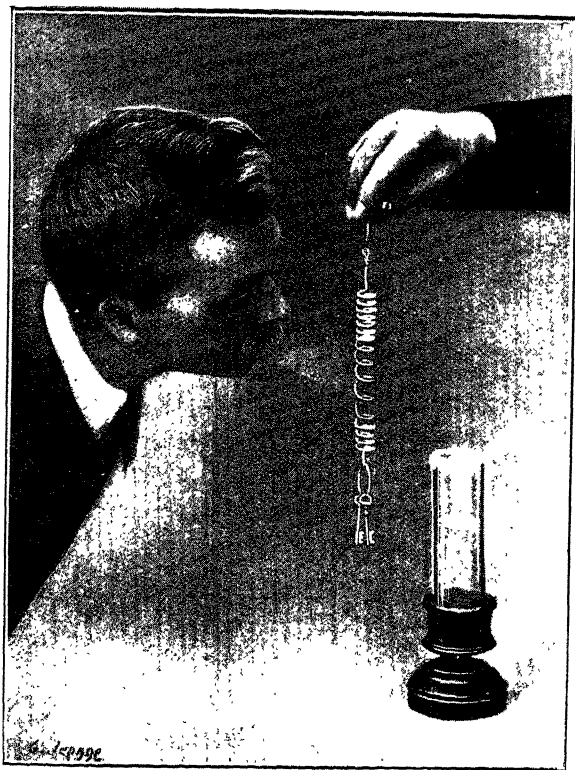


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## PROPERTIES AND PHYSICAL EFFECTS

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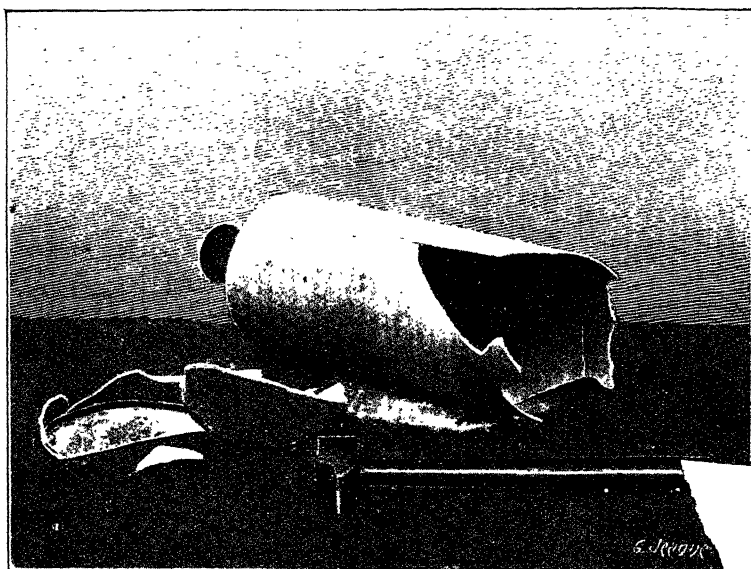


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### FREEZING OF LIQUIDS: MERCURY, ALCOHOL, ETC.

As a matter of course, at these ultra-Siberian temperatures, almost all the liquids which we know take on the solid state. Mercury becomes frozen with an ease which

s almost laughable, for against the  $-40^{\circ}\text{C}$ . which it calls for, we have  $-190^{\circ}\text{C}$ . to dispose of. And it is not at all commonplace, as you can see here (Figs. 93 and 94), to drive nails with a hammer of quicksilver cast in a test-tube, or—singular association of ideas!—to pulverise the india-

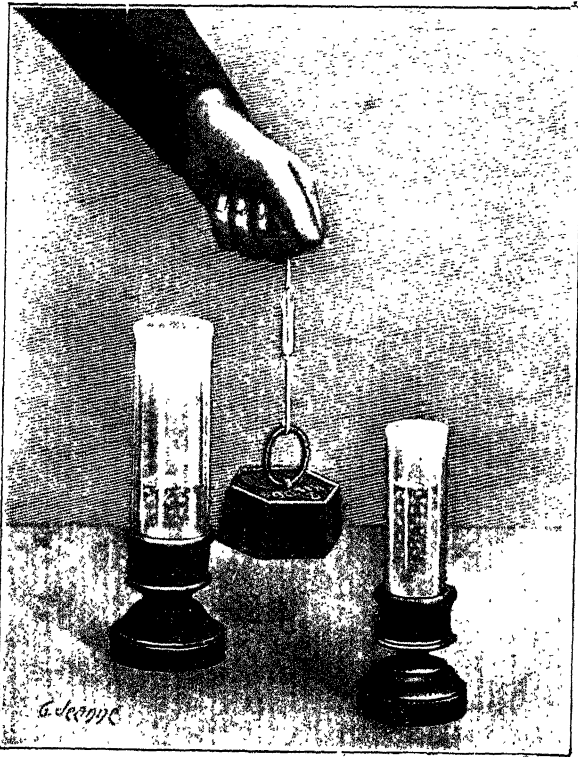


FIG. 91.—Experiment on the increased resistance to tension in metals.

ber with which we were experimenting with this mercury hammer!

Proof alcohol itself, which was considered once upon a time as very refractory to freezing, loses all right to this reputation, because it has acquired the hardness of a stone, long before the temperature of liquid air.



The experiment may be tried by submerging a test-tube containing a little alcohol in liquid air.

At the end of an instant, the alcohol, which is at first syrupy, is transformed into a crystalline block.

If we replace the alcohol of the above experiment by

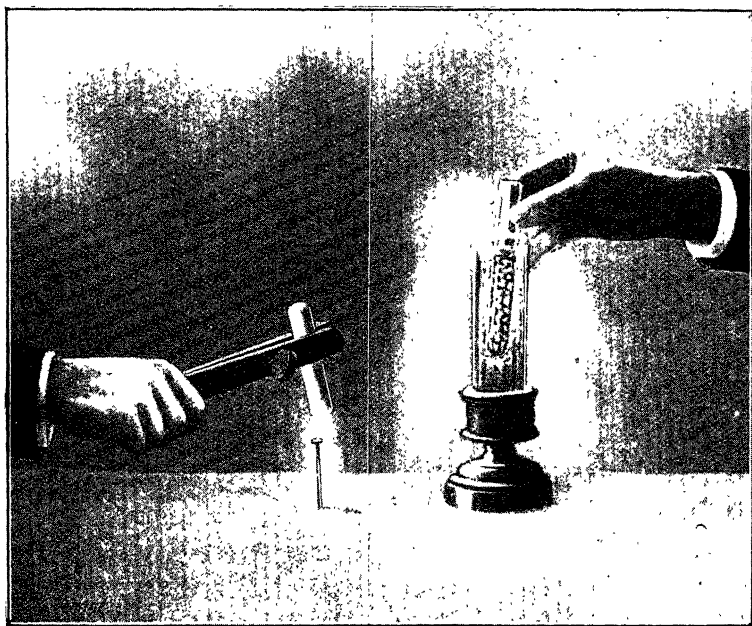


FIG. 92.—Experiment on the increased resistance to tension in metals.

rum, anisette or Chartreuse—placing them for fear of breakage in metal goblets, which, by means of a string, we can plunge half-way into liquid air until the remarkable thickening, which is the first stage to solidification, become apparent. We can in this fashion obtain a kind of paste which we can extract with a spoon, and which we can swallow, if we like, without disagreeable effects, notwith-

standing its very low temperature, thanks to the low specific heat of alcohol, and thanks also to the anæsthetic effect of low temperatures, whose peculiarities we have already pointed out (p. 35).

In this way we obtain iced drinks, which Brillat-Savarin would not have disavowed, and which deserve to become the fashion, if this halting excursion into the realm of *middle-class cookery* be permitted us.



FIGS. 93 and 94.—Manufacture and use of an uncommon hammer.

**Case of petrol-ether; d'Arsonval's experiments; liquid thermometers.**—Almost the only one among liquids, petrol-ether or gasolene, has the courage of its qualities in the presence of liquid air, and can resist congelation. We have seen above that Claude had the idea of putting this remarkable property to use to ensure the lubrication of machines with moving parts used in the manufacture of liquid air.

It can also be applied to the construction of ordinary thermometers to replace the electric thermometers which are habitually used to determine low temperatures, and especially that of liquid air.

But, for such uses in connection with thermometers, it is essential that the liquid should be absolutely uncongelable, and the rectifications to which we subject petroleum, in manufacture, to obtain petrol-ether would be insufficient for a really good result.

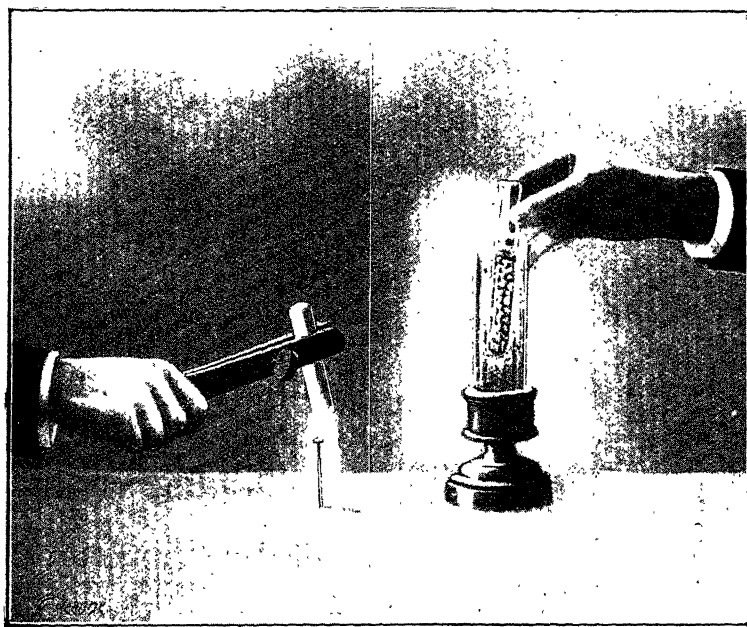
D'Arsonval devised for this object a most elegant method of purification, and which is capable of being applied equally to the separation of different gases, and to thus furnish a very valuable method of analysis. We quote his own words: the "*sang froid*" with which he puts forward the most disconcerting ideas is most suggestive.

"The process is extremely simple, as the petroleum can contain in solution certain hydrocarbons which are condensable at low temperatures. The first thing to do is to separate out these gases. We start, therefore, by placing these petroleums *in vacuo*; with a suction pipe the gases in solution are removed, then we proceed to a first congelation in methyl chloride at  $-23^{\circ}$  C. to separate out the benzine. To separate out the other products whose points of fusion are still lower, the petroleum is then plunged in a mixture of acetone and carbonic acid snow at  $-80^{\circ}$  C., and in this way we manage to condense another series. Finally, if we place the recipient containing the petroleum at  $-80^{\circ}$  C. in communication with a recipient plunged in liquid air at  $-190^{\circ}$  C., so as to distil the petroleum at  $-80^{\circ}$  C. by heating, and condensing the vapours at  $-190^{\circ}$  C., we shall obtain liquids which are wholly uncongelable in liquid air and may be used in the construction of thermometers for very low temperatures."

Heating petroleum at  $-80^{\circ}$  C. is certainly not an usual expression, and many of our readers will not fail to be non-

standing its very low temperature, thanks to the low specific heat of alcohol, and thanks also to the anæsthetic effect of low temperatures, whose peculiarities we have already pointed out (p. 35).

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**Case of petrol-ether; d'Arsonval's experiments; liquid air thermometers.**—Almost the only one among liquids, petrol-ether or gasolene, has the courage of its qualities in the presence of liquid air, and can resist congelation. We have seen above that Claude had the idea of putting this remarkable property to use to ensure the lubrication of machines with moving parts used in the manufacture of liquid air.

It can also be applied to the construction of ordinary thermometers to replace the electric thermometers which are habitually used to determine low temperatures, and especially that of liquid air.

But, for such uses in connection with thermometers, it is essential that the liquid should be absolutely uncongelable, and the rectifications to which we subject petroleum, in manufacture, to obtain petrol-ether would be insufficient for a really good result.

D'Arsonval devised for this object a most elegant method of purification, and which is capable of being applied equally to the separation of different gases, and to thus furnish a very valuable method of analysis. We quote his own words: the "*sang froid*" with which he puts forward the most disconcerting ideas is most suggestive.

"The process is extremely simple, as the petroleum can contain in solution certain hydrocarbons which are condensable at low temperatures. The first thing to do is to separate out these gases. We start, therefore, by placing these petroleum *in vacuo*; with a suction pipe the gases in solution are removed, then we proceed to a first congelation in methyl chloride at  $-23^{\circ}$  C. to separate out the benzine. To separate out the other products whose points of fusion are still lower, the petroleum is then plunged in a mixture of acetone and carbonic acid snow at  $-80^{\circ}$  C., and in this way we manage to condense another series. Finally, if we place the recipient containing the petroleum at  $-80^{\circ}$  C. in communication with a recipient plunged in liquid air at  $-190^{\circ}$  C., so as to distil the petroleum at  $-80^{\circ}$  C. by heating, and condensing the vapours at  $-190^{\circ}$  C., we shall obtain liquids which are wholly uncongelable in liquid air and may be used in the construction of thermometers for very low temperatures."

Heating petroleum at  $-80^{\circ}$  C. is certainly not an usual expression, and many of our readers will not fail to be non-

plussed by this extraordinary process of distillation. •It is, however, the exact truth, as they will see by recalling what we have stated before. So long as a body is not at  $-273^{\circ}$  C. it is relatively hot, and may, therefore, serve as a source of heat in respect of a colder body than itself. It is, however, no source of heat for our bodies, that is certain!

**Extraction of new gases from the atmosphere; work of Sir William Ramsay; liquefaction of helium.**—Moreover, it was by identical means, by submitting liquid air itself to fractional distillation, that it was possible to separate out those new gases of the atmosphere, whose discovery has constituted one of the scientific triumphs of the last few years. Certainly, it is extraordinary that for such a length of time we should have lived under the idea of the simplicity of an atmosphere which is really so strangely complex. What is stranger still, perhaps, is that the honour of having revealed this complexity, of having discovered the various elements which enter into the composition of atmospheric air, should belong to a single scientific man, to the illustrious Sir William Ramsay, whose theories on the transformation of matter have in our day turned the whole of science upside down.

It is, moreover, Sir W. Ramsay, who, considering for the first time with Lord Rayleigh the singular discrepancy already pointed out by Leduc between the density of atmospheric nitrogen and chemical nitrogen, was led to the isolation of *argon*, whose proportion in the atmosphere is not less than 1 per cent.—an enormous proportion which fixes the amount of this gas present in the terrestrial atmosphere at 50 trillions of tons!

It is Ramsay who discovered in the gas of cleveite the element which the spectroscope had already indicated in the sun, *helium*, whose existence in our atmosphere was afterwards determined by Sir J. Dewar, and which, following upon the work of Ramsay himself, appears to be the

latest result, so to speak, of the manifestations of radio-activity which we find at the present day, at every turn on our globe.

It is again Ramsay, with his collaborators Collie, Travers and others, when subjecting the gaseous residua of Hampson's machine to a delicate fractional distillation, who found *neon* in the first stages of the distillation besides *helium*, and who isolated in the final stages both *krypton* and *xenon*, other inert gases which are absolutely unique because of their enormous atomic weights, 80 and 160, which are multiples of that of argon, and places them as gases much denser than air, with densities of 2.80 and 5.60.

Notwithstanding the small quantities of liquid which were available for this work of separation, this distillation was carried out with such marvellous precision that Sir W. Ramsay found it impossible ultimately to find other elements in the residue of the liquid obtained from 100 tons of air, which Claude was able recently to place at his disposal. We may, therefore, assume that our knowledge of the composition of the air is definitely fixed, at least on the side of the less volatile elements, and the illustrious scientist has not failed to deduce from this fact the most interesting conclusions.\* All these bodies, in point of fact, furnish science with many points of interrogation. They are all monatomic bodies, the only ones which, besides mercury, are clearly such, with feeble chemical affinities, to the extent that up till now it has been impossible to make them enter into any clearly defined combination. Their spectra are magnificent, especially that of neon, which yields in Plücker tubes a very intense light the colour of fire.

Helium is the most refractory of all known gases to liquefaction, although its atomic weight and its density,

\* French Association for the Advancement of Science; Clermont-Ferrand, August, 1908.

which is double that of hydrogen, might have led us to hope for an easier liquefaction. It is only quite lately that Professor Kamerlingh-Onnes has succeeded in liquefying it by means of an apparatus which is a marvel of ingenuity and construction, under the influence of a preliminary refrigeration with boiling hydrogen *in vacuo* and of expansion from 100 atmospheres.\*

On the other hand, this resistance to liquefaction appears to be a common characteristic of these new gases, a characteristic doubtless attributable to their monatomic character, for argon, for example, although denser than oxygen, only liquefies under atmospheric pressure at 5° C., less, that is, at - 186° C.†

Moreover, the extraordinary relations determined by Sir W. Ramsay between these various gases and the emanations of radium, which yielded, according to circumstances, helium, argon or neon, increases still more powerfully the interest which attaches to this category of gases, which, according to the determinations referred to above, fixes very approximately as follows their proportion in the air.‡

Helium	1 to 2	.	.	.	.	per 1,000,000 of air
Neon	1 to 2	.	.	.	.	" 100,000 "
Argon	0.937	.	.	.	.	" 100 "
Krypton	1.0	.	.	.	.	" 1,000,000 "
Xenon	1.0	.	.	.	.	" 30,000,000 " §

**Congelation of gases; commercial preparation of hydrogen.**—If liquid air disturbs profoundly the cohesion of metals, and solidifies, excepting the ether of petroleum, the

\* Helium presents itself under the form of a transparent colourless liquid, boiling at - 269° C. with the density of 0.154. Its critical constants appear to be close to - 268° C. and 3 atmospheres ('Transactions,' August 24th, 1908).

† The boiling-points of neon, krypton and xenon are respectively - 288° C., - 152° C., - 109° C.

‡ Travers, 'Study of Gases,' 1901, p. 106.

§ Or in 170,000,000 according to the last determination of Sir W. Ramsay.



most refractory of liquids, it obviously acts with equal energy on gases themselves.

The majority of these—sulphuric acid, chlorine, carbonic acid—are not only liquefied, but solidified by contact therewith. Hydrogen, however, because of its temperature of

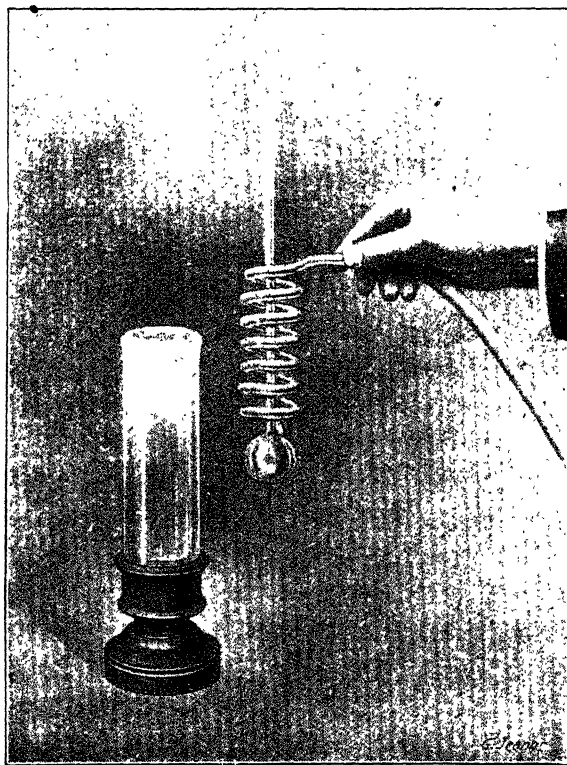


FIG. 95.—Experiment addressed to aeronauts.

liquefaction, is absolutely refractory to the effect of liquid air. Hence an ingenious means pointed out by d'Arsonval for the easy preparation of hydrogen from lighting gas, one half of whose volume consists of this gas.

A worm (Fig. 95) is traversed by a stream of gas, which is set light to. The worm is plunged in a test beaker

filled with liquid air: the flame gets shorter, paler, and you can then distinguish the flame of hydrogen. All the other components, with the exception of a little carbonic oxide, are condensed in a whitish film on the internal wall of the worm. This solution would evidently be uneconomical and far from handy when applied on a large scale because of the recurring obstacles due to the accumulation of solid matter in the feeding circuit; an obvious variant is preferable consisting in substituting *simple water gas* for lighting gas; this is very cheaply produced in manufactures and in this the liquefaction of carbonic oxide alone is necessary. Claude has already carried out some very hopeful experiments in this direction,\* and Dr. Linde has on his side devised and realised an apparatus applying it in a continuous fashion, with only a few drawbacks due to impurities, for the separation of 10 cubic metres of hydrogen † and 10 cubic metres of carbonic oxide per hour.

This question, at the present epoch of unlimited aerosation, may become very important, because the price of hydrogen, which amounts at present to 1 franc per metre cube for all atmospheric navigation, might be produced so as to cost less than *half* this price.

**Congelation of the air.**—Not content with congealing liquids whose refractoriness is the most notorious, liquid air is capable of freezing itself. We have seen already that under a pressure of 0·07 of an atmosphere, which can easily be obtained with an ordinary air-pump, the temperature of liquid nitrogen falls to  $-213^{\circ}\text{C}$ . Now  $-213^{\circ}\text{C}$ . is the temperature of freezing for nitrogen. Therefore if we connect a recipient with double walls containing liquid air to a

\* See 'Transactions of the Aeronautic Congress of Brussels,' 1907.

† Another important use for cheap hydrogen has already arisen in connection with the manufacture of synthetic ammonia. The Badische Anilin Soda Fabrik have in course of erection a huge plant for this purpose, in connection with which the Linde Ice Machine Co. of Munich are supplying one of their largest nitrogen plants (1912).

good pump, and we scrupulously remove the vaporised gas which results from lowering the pressure, the liquid air very soon is replaced by a colourless frozen mass through the solidification of *the nitrogen*.

A curious circumstance, however, is this; although oxygen liquefies easier than nitrogen, it solidifies far less easily, and it is only in the neighbourhood of  $-225^{\circ}\text{C.}$  that it finally passes into the solid state.

The nitrogen thus solidified, freed by compression from the liquid oxygen which it holds, is sensibly pure. All these facts have been known for a long time.\* A German inventor, Erdmann, has contended that this method would permit of the manufacture of very pure nitrogen, required for the artificial production of nitrogenous products, at a very low price. This would be, strictly speaking, going round the corner with a vengeance, because it is extremely improbable that a process which requires frightfully low temperatures and very perfect vacua, and the scrupulous cleansing of solid nitrogen, which, moreover, cannot reasonably be easily adapted to continuous working, can attain the requisite economy to hold its own with the simple processes for obtaining pure nitrogen which we are going to describe (p. 370).

If we repeat the above experiment with a simple test-tube holding liquid air, and connected with a vacuum pump (Fig. 96), another very curious consequence of the lowering of temperature thus obtained, can be observed. The external air which is in contact with the walls of the tube is *liquefied* by the effect of this cold, of  $-200^{\circ}\text{C.}$  and over, and this is only reasonable, since its temperature of liquefaction at atmospheric pressure, its *dew point*, is only  $-192^{\circ}\text{C.}$  It thereupon flows down the surface of the tube, and it is not a sight devoid of interest to see air, which is habitually so refractory to liquefaction, "weeping,"

\* See 'Liquid Air,' by G. Claude. Publisher; Demod, Paris, 1903, p. 86.\*

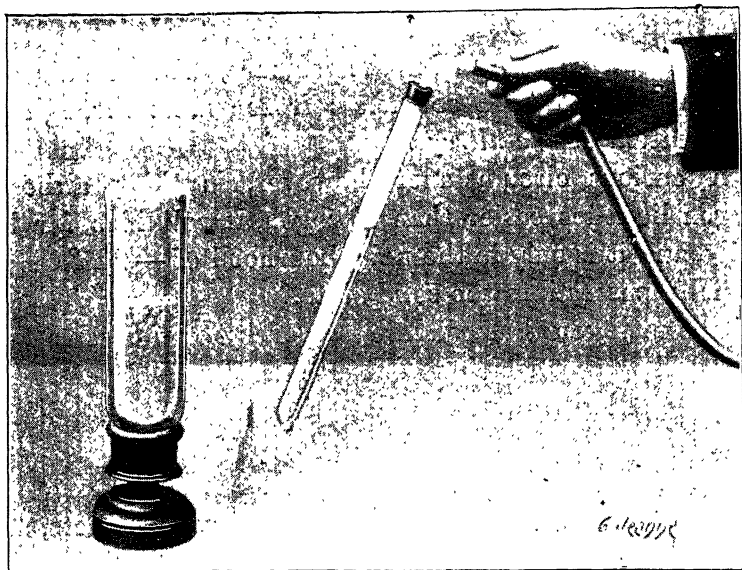


FIG. 96.—Pitiable behaviour of an erstwhile permanent gas.



FIG. 97.—Curious behaviour of a metal bottle half filled with liquid nitrogen.

as easily under the circumstances as water vapour, which in winter flows down the windows of our rooms.

The exactitude with which the previsions of theory are realised in all these phenomena is such that the same phenomenon is reproduced in a very curious way and without any complications in the case of liquid nitrogen, although in this case the temperature of liquid nitrogen, —  $195^{\circ}\text{C}$ ., only differs by  $3^{\circ}\text{C}$ . from the dew point of air. If we half fill a metal bottle with this liquid nitrogen, which can be obtained very easily, as we shall see, in a Claude apparatus (p. 372), we shall observe, in point of fact, that the external surface of the bottle gets covered with ice over all the portion below the internal level of the liquid nitrogen, and on the contrary is completely wetted with liquid air over the whole of the bottle below that level, as if the bottle were porous and allowed the liquid it contained to filter through! The internal level is as apparent as if the bottle were transparent, and the moistened portion, which is clearly divided from the white of the icing, follows all the fluctuations of the internal level, as the figure indicates when the bottle is given various inclinations.

The white stain below the bottle is caused by the rime resulting from the evaporation of the liquid air, which flows abundantly over the table where the experiment is made.

**Properties of charcoal at the temperatures of liquid air; the commercial production of high vacua.**—The work of Professor Dewar has added a very interesting chapter to the properties of liquid air.

We have already had occasion (p. 225) to admire the process invented by this celebrated English scientist for obtaining high vacua by the aid of liquid hydrogen, but we had to point out that, till further orders, this process was hardly practical, because of the difficulty of obtaining this liquid hydrogen. But in the course of his researches Sir

James Dewar has discovered a solution which is preferable in quite another way, since by its means it is possible to attain the highest vacua with *liquid air*, which is immeasurably more useful.

This solution depends on the extremely curious fact that at very low temperatures *wood charcoal* has its well-known absorbent properties for gases increased in so extraordinary a measure that this absorption may be extended to the extreme limits of vacua.

Dewar has signalled out, as specially adapted for this object, coconut wood charcoal, but the ordinary breeze of the baker yields excellent results, provided it has been properly calcined and effectually deprived of moisture. He has also found that certain other powdery substances possess similar properties to a minor degree.

The following experiment, carried out with a small apparatus devised by Messrs. d'Arsonval and Claude, shows very clearly the extraordinary capacity for absorption of charcoal, and certainly constitutes in addition, one of the most beautiful and instructive experiments in physics.

A very partial vacuum, equal to 2 or 3 mm. of mercury, is produced in a Crookes' flask (Fig. 98) by means of a simple hand-pump. Because of the partial vacuum the electric discharge between the electrodes presents the special violet look which constitutes the first step between ordinary sparking and the phenomena of a Gessler tube. The tube is mounted on the apparatus of which we have been speaking. It can be put in communication by one of the two valves of the apparatus with a metal recipient full of wood charcoal, which is immersed in liquid air.

If we thereupon establish through this valve the communication in question, the air is absorbed with avidity, and you see, as a consequence, the magnificent phenomena of a Gessler tube rapidly succeeding each other,

But the vacuum is still increasing, and the superb yellow-green fluorescence of the glass becomes apparent under the shocks of the mysterious projectiles emitted by the cathode at the somewhat lively velocity of 30,000 kilometres per second—sufficient to encircle the globe between

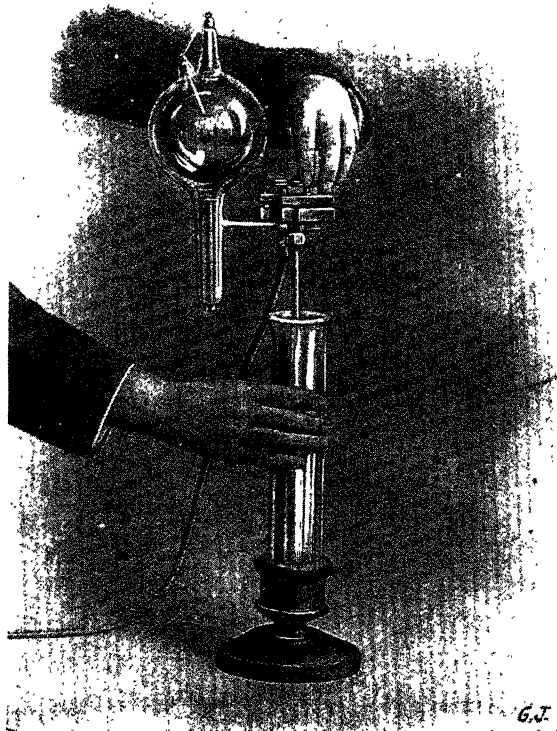


FIG. 98.—Experiment on the production of very high vacua.

two heart beats! The fluorescence increases; it soon extends to the whole hemisphere touched by the cathode emanations. The apparatus is now transformed into a flask well adapted to radiography. Then the phenomenon progressively decreases. The tube *hardens*, as radiographers would say,

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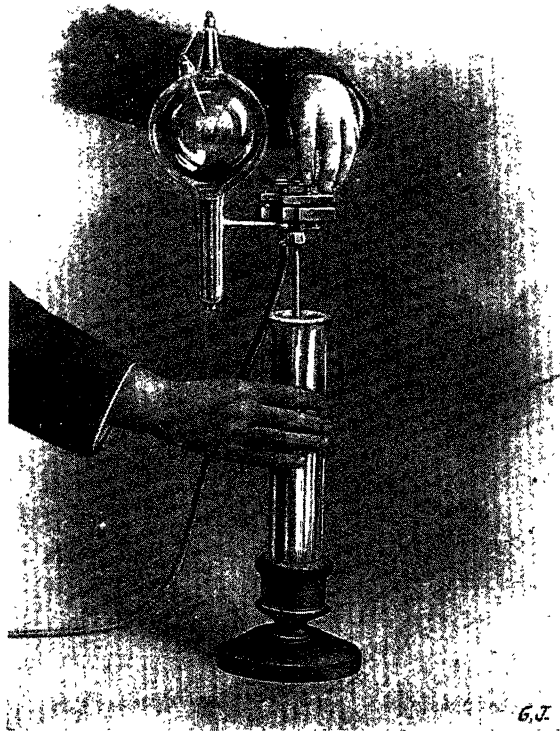


FIG. 98.—Experiment on the production of very high vacua.

two heart beats! The fluorescence increases; it soon extends to the whole hemisphere touched by the cathode emanations. The apparatus is now transformed into a flask well adapted to radiography. Then the phenomenon progressively decreases. The tube *hardens*, as radiographers would say,

and then is extinguished; this means the tube is now so *hard* that the electric discharge can no longer traverse it; the charcoal has, in fact, taken us without trouble to the inconceivable vicinity of one ten-millionth of an atmosphere.

The air is thereupon re-admitted by the other valve, and you see the same series of magnificent phenomena repeat itself in inverse order. By stopping the admission of the air to the Gessler vacuum and re-opening the valve communicating with the charcoal we can effect a second absorption, and so on, the duration of each absorption under favourable conditions being barely three minutes for a flask of 1.5 litres, which is equivalent to an effect incomparably more energetic and more rapid than that of an air-pump.\*

This remarkable property being certainly susceptible of being used industrially, it appears of interest to insist somewhat on the results obtained by Claude.

With a quantity of charcoal of only 15 gs. the absorptive capacity is such that according to Claude's experiments it is possible to effect twenty-five absorptions one after the other in a 1.5, l. flask, starting on each occasion from 5 millimetres pressure and ending with a spark equivalent to 20 centimetres in length. Each of these successive exhaustions is governed by a rather curious law of variation in the length of the equivalent spark as a function of the law of time which is shown on Fig. 99, where we see that the sparking distance takes a certain time to become apparent, and where, starting from 1 centimetre, the equivalent spark grows with extreme rapidity up to the maximum length of which the coil is capable. These facts are capable of furnishing interesting data on

\* In reality the "preparation" of the flask is more troublesome than has been indicated, because its walls and its electrodes *emit* from the first during the passage of the current and for a very long time.

the mechanism of the electric discharge. After the twentieth operation, the air absorbed by the charcoal commences to acquire a certain tension; more time is required to reach extinction. After twenty-five operations it can no longer be attained. At the sixtieth operation we

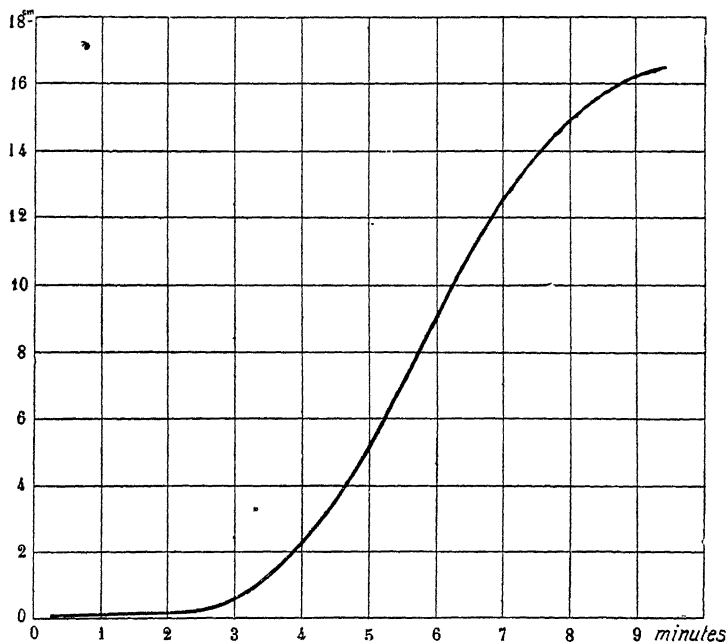


FIG. 99.—Variation in the resulting length of spark as a function of the time.

cannot even obtain 1 centimetre of equivalent spark. At this stage the 15 gs. of charcoal have absorbed

$$\frac{60 \times 1500 \times 3}{760} = 600 \text{ cubic centimetres}$$

of air measured at atmospheric pressure, and this at a final pressure of barely 1 centimetre of mercury. Of this enormous absorption, about 250 cubic centimetres have been absorbed with a tension lower than that of a Crookes' vacuum! These results are due to the cooling with liquid oxygen; they are notably improved further with air and

still further with liquid nitrogen in consequence of the lower temperatures.

When the charcoal is saturated it can be regenerated quite simply by bringing the recipient which holds it back to the ordinary temperature and heating it under reduced pressure to 100° or 200° C. It seems capable of being used again in this way a great number of times.

In the course of these experiments Claude made a very curious observation which requires for its successful repetition that the Crookes' tube with which you operate should not be obscured by long use. At the moment at which, through the action of the charcoal, the Crookes' tube has reached the degree of exhaustion designated by radiographers as "soft," if any point of the surface of this tube be touched by waste filled with liquid air, the tube is *instantly extinguished*, the equivalent spark then passing suddenly to the maximum length to be attained by the coil. This very interesting experiment seems to prove that as far as the slight gaseous residue is concerned remaining in the tube, and which permits of the discharge, the glass of the flask possesses to a slight degree the same condensing properties as charcoal.

Singular fact, however, when the tube is not new, this effect is much reduced, to the extent that it no longer occurs if the tube has been obscured by long use.

**Possible applications of these charcoal properties; metallic recipients for liquid air; manufacture of oxygen in the vicinity of waterfalls.**—A process for obtaining high vacua as marvellous as the one which we have been describing, will certainly not remain without manufacturing applications, in connection with which, at present, the so to speak perfect exhaustion, required in particular for incandescent lamps, Crookes' tubes and Cooper-Hewitt tubes, is produced with such difficulty.

An application particularly indicated and suggested

by Dewar immediately after his discovery was the obtaining of the vacua in the liquid air recipients themselves; it is not impossible that we should thus find the means of finally saving ourselves from the absurd fragility of the admirable Dewar-d'Arsonval recipients which limit in such a provoking way the possible uses of liquid air. If such recipients cannot be manufactured of metal, it is because the porousness of this material can hardly ever be strictly avoided any more than the occlusion of gases in the walls, and that the vacuum as a consequence, cannot subsist

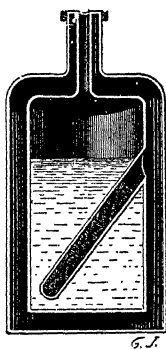


FIG. 100.—Recipient for liquid air of metal which utilises the properties of charcoal.

indefinitely in the recipient with the high degree of perfection which is indispensable.

But suppose that a T-tube full of carbon has been placed in the internal walls of a metallic recipient disposed as shown in Fig. 100; supposing an initial vacuum has been produced as carefully as possible in the intervening space, and therefore at the same time on the carbon: when the recipient is filled with liquid air the charcoal will find itself in this way immersed, and will act automatically to maintain the vacuum in spite of the slow re-entrance of air which might occur. Claude has been able on this principle to make some copper recipients of 5 litres capacity which preserved liquid air for almost a week, but he gave up

their manufacture to avoid an infraction of Professor Dewar's patents, on whom it is incumbent therefore to see that the manufacture of liquid air benefits by his beautiful discovery.

With recipients of this kind of large dimensions and arranged as tank-wagons, it will be, for example, possible to manufacture liquid oxygen at extremely low price in the vicinity of waterfalls, and transport it by rail, with a very small loss, to centres where it is used, and where its evaporation with accompanying liquefaction, following the principles laid down in the fourth part of this work, will furnish us at one and the same time with motive power from gaseous oxygen and cold.

We shall be able also, as suggested by Dewar, to secure by the same means vacuum envelopes for the liquid air apparatus.

Finally, in a more scientific direction, it is also due to this property of charcoal that we owe our knowledge of the existence of helium in our atmosphere. Dewar, in fact, determined that charcoal absorbs not only oxygen and nitrogen, but argon and neon and the various other gases with the exception of helium; this is not astonishing, since the facility of absorption depends according to all appearances upon aptitude for liquefaction, and we know that helium in this respect is the most refractory of all gases. Now Professor Dewar, having absorbed as completely as possible the atmospheric air, found in the unabsorbable residuum the spectrum of helium.

**Specific heat of bodies at low temperatures.**—A fact of an entirely different order, less interesting no doubt from a superficial point of view, very important, on the contrary, from the scientific and practical standpoint, is the following.

In the course of experiments made with the object of submitting bodies to the very low temperatures furnished by liquid air, we have been led to determine that the

calorific capacity of these bodies suffers important modifications in the course of lowering the temperature.

Metals, according to Behn's experiments, have their specific heat notably diminished, and this diminution increases with the lowering of the temperature to such an extent that in the neighbourhood of the absolute zero a very little heat added to or subtracted from a metallic mass will suffice to modify its temperature considerably.

Gases, on the contrary, have their specific heat,

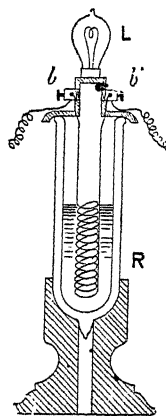


FIG. 101.—Experiment upon the lowering of the resistive power of metals at low temperatures.

especially when under pressure, augmented. We have even noted the enormous importance of this fact when discussing the various methods of liquefaction (p. 140).

**Electrical resistance and magnetic properties of metals at low temperatures.**—An extremely remarkable effect of the same order as the preceding, is the enormous diminution which pure metals experience in their electric resistance at the temperature of liquid air. The resistance of a copper wire, for example, falls to a *fiftieth* of its amount. Whence the experiment we detail here (Fig. 101).

Here is an electric circuit constituted by a few accumu-

lators, an incandescent lamp, and a copper coil of sufficiently high resistance. The dispositions are so made, that if the circuit is closed the filament of the lamp hardly glows at all. But if the coil is plunged in liquid air, through the fall in resistance produced the lamp produces a dazzling white light.

At first blush we might think this fact as devoid of all practical importance.

Elihu Thomson, soaring to the summit of joking without turning a hair, has, nevertheless, proposed to utilise this to reduce in a large measure the enormous quantities of copper used up in the great cables for modern electrical installations. By arranging to have these cables immersed in liquid air it would be possible to reduce their section, as well as obtain, on the drop of potential in the transmission, a sufficient economy of current to restore the liquid air lost through evaporation.

As he was about it, the learned American engineer might as well have proposed for this purpose the startling use of liquid hydrogen. With this substance, in fact, which boils at  $-252^{\circ}\text{C}$ ., it is even quite another matter than with liquid air; if electricians should have the good fortune to work at these low temperatures they might transmit their current through cables a *hundred times* smaller, with equal loss of potential, than those which they are obliged to use at the present time. This would probably put a stopper on the falls of the *Rio*.

In the absence of immediate practical interest, the theoretical interest of these facts is very great. They seem, moreover, to corroborate a rather hazardous hypothesis of Ampère, according to which the resistance of metals to the electric current does not appear, save when passing the intermolecular spaces. At the absolute zero, these spaces no longer exist because of contraction; the electric resistance of pure metals should therefore be *nil*, and it is



exactly what, excepting a very perturbing anomaly at the temperature of liquid hydrogen, experience seems to confirm.

Curious thing, while the electric resistance of metals is subject to such enormous variations, the magnetic properties of iron and steel hardly vary at all at low temperatures. Claude demonstrated, in 1899, that a sample of soft iron presented very closely at  $-190^{\circ}\text{C}$ . the same permeability as at the ordinary temperature, and that hysteresis is hardly modified at all.\*

Exceptionally, however, certain samples of hard iron had their permeability quintupled under the action of feeble magnetising forces.

Besides this, Messrs. Guillaume and Osmond have determined that certain samples of a metal which possessed some very singular properties—*e. g.* nickel steel—presented the peculiarity of becoming magnetic at low temperatures, and that certain of them even preserved indefinitely the magnetic properties thus acquired.

As a last interesting comment on this chapter, let us note in addition that one of the most efficacious ways of *setting* magnets, *i. e.* to impart to them the fixity of magnetisation, indispensable to their use with instruments for electric measurements, consists in repeatedly dipping them in liquid air.

**Changes of coloration: Phosphorescence.**—Finally, to complete the series of principal phenomena that liquid air provokes by its temperature alone, we must mention that the molecular contractions which accompany the immersion of bodies in liquid air occasionally give rise to curious changes of coloration.

A sheet of paper reddened with bi-iodate of mercury becomes yellow when dipped in liquid air. It re-acquires, however, its primitive colour when it becomes warm again.

\* 'Transactions,' August 21st, 1909.

A red pencil suffers the same temporary modification owing to the vermilion it contains. If some economical manufacturer had used minium to produce the colour we could not depend upon liquid air to discover the fraud, because in this respect minium behaves exactly in the same way as vermilion.

It should further be noted that paraffin, eggs and many other substances become slightly luminous in liquid air, through a phosphorescent effect which naturally cannot be seen except in a completely darkened room.

**J. Becquerel and P. Lebeau's experiments, etc.**—We think it interesting to mention in this connection the services which liquid air can render in laboratories, such as, more especially, it was able to render quite recently to the young representative of an illustrious name, in some most interesting researches. Without entering into the details of those experiments, whose description would lead us beyond the limits of this work, let us state that the discoveries made by J. Becquerel on certain inversions of Zeemann phenomena at the temperature of liquid air have become the starting-point of conceptions capable of strongly illuminating our ideas concerning the theory of electricity and the constitution of matter.

In quite another range of ideas, Lebeau, professor of the School of Pharmacy, has found in liquid air an experimental aid of the highest convenience, and was successful by its use in solving certain delicate problems relating to the separation of gaseous mixtures. D'Arsonval and Bordas have devised a very convenient means for the desiccation of serums based upon the vacua produced by liquid air and charcoal, etc.

It would be very desirable that the technics of the use of liquid air, from which Sir William Ramsay obtained, on his side, the marvellous results which we know, were better known to chemists, who would often, thereupon,

have reason to congratulate themselves. The difficulty here, as in all other cases, is the fragility of the recipients.

**Application of liquid air to shrinking on of bands and hoops.**—We all know the process, which is utilised in manufactures to shrink on the bands on cannon and other objects, and which is even applied in the country by blacksmiths, who shrink on iron tyres on the wheels of vehicles to protect them; the tyre of the wheel is strongly heated and is fitted to the wheel by the expansion thus obtained, and the eventual cooling produces a very powerful shrinkage.

Now the requisite difference of temperature can in certain cases, and particularly in the case of fragile objects, be obtained in a more convenient way by contracting with liquid air the object to be hooped or banded; to still further increase the difference in temperature, the subsidiary piece can, if there be no objection, be slightly heated. It is easy, for example, to forcibly fit by this means metallic tubes into tubular plates which have been pierced with too little play.

This application was suggested to Claude by his regretted master, E. Hospitalier.

**Application of liquid air to the production of motive power.**—We have seen above what considerable pressures liquid air can develop on closed vessels containing it, under the sole action of the heat of the environment. The idea was—invariably conceived—of using these pressures so easily produced for developing motive power. *A priori*, the idea may be attractive. What a marvellous source of energy should this liquid air be which the heat of the environment suffices to evolve! No more fire, no more smoke, no more bad smells, no more nerve-shaking noises of explosion motors. What a dream, ye gentlemen motorists, and with what eagerness you would give up, at the price of so many improvements, your claim to the title of *chauffeur*, which would have thereafter become the reverse of the fact!

And how little, nevertheless, would all this count in

comparison with other consequences of such a sensational application!

They do not omit to remind us, either, that this heat of the environment which would suffice for working these liquid air motors, this free heat, *costs nothing*. The atmosphere surrounding us, the water of the seas and rivers, each fragment of terrestrial matter, contains inexhaustible stores thereof, which the sun, with never-failing care, is always renewing. To all the qualities enumerated above, the source of energy in question would add the inestimable characteristic of being *gratis*. *Gratis*—save for the liquid air, be it understood; but, truly, this is something which should not trouble us much, since the motive power produced by a little liquid air is so enormous that by its means we could easily liquefy *a little more*. It is Tripler, the great American liquefier, who has been putting forward these conundrums probably with the object of enthusing capitalists, and of liquefying—some of their millions. The manes of Keely, of celebrated memory, should be shuddering with envy.

All this, however, is not serious business, and we may be permitted to charitably warn our automobile aspirants that if they purposed, on the strength of all these attractive tales, to await the advent of liquid-air motors to take to the road, they will run a great risk of running over no one for a long time.

Let us reason it out.

For the eccentric prophets, who, in spite of the most uncompromising principles of thermo-dynamics, would pretend to solve, thanks to liquid air, all the problems involved in the production of motive power, all the difficulties of automobilism and aviation, this liquid would appear to be very generally an unequalled accumulator of energy. Now, in thinking thus, they deceive themselves; and they deceive themselves even twice over.

Firstly, liquid air, no more than any other liquefied inert gas, is in no sense of the term an accumulator of mechanical energy. Quite the reverse. We know, moreover, that, in point of fact, liquid air is nothing more than ordinary air from which calorific energy has been *subtracted* to bring it down to the low temperature which characterises it. Therefore it does not hold in itself any utilisable energy, and, if it undoubtedly brings any into play during its expansion, it is indispensable that it should borrow some in the form of heat from the environment during both its evaporation and its expansion.\* It is, therefore, at most an intermediary—an intermediary which permits of the transformation of the heat of the environment and its manifestation in a mechanical form.

But we would not cavil over so little if, at least, it was an intermediary capable of great things. The misfortune is that it is nothing of the kind, and if, by applying an elementary formula of thermo-dynamics, we estimate the mechanical energy which it can bring into play during expansion, even supposing that this is wholly completed isothermically at the ordinary temperature, we shall find—

$$W = P_0 V_0 \cdot \text{Log}_e \frac{P_0}{P_1} = 8000 \text{ Log}_e 800 = 53,300 \text{ kilogramme metres; or}$$

$$\frac{53,300}{270,000} = \frac{1}{5} \text{ of a H.P. hour per kilogramme of liquid air expended.}$$

This is rather insignificant.

And even if we should admit that, by an extraordinary piece of luck so far unknown to constructors, we should be able to use up this very precious energy down to the last drop, this one fifth of horse-power hour, which each kilogramme of liquid air could then part with to the mechanism of the new type of automobile, still would not represent

\* It is for analogous reasons that compressed air, although used for the production of motive power in tramway traction, is not at all an accumulator of energy, as many engineers imagine, forgetful of Joule's famous law.

more than the *tenth part* of that which, without any trouble, petrol can furnish. A fine business indeed, and truly a well-selected motor to propel the aviator of our dreams through the air.

So, then, we may renew the discussion of the employment of liquid air as a source of motor power, when its cost is one tenth that of petrol and one fiftieth of that of coal. And from now till that time arrives, we may rest confident that much dirty water will still flow under the bridges!

It will possibly be objected to the above reflections that a cab moved by liquid air has actually run for some time in the streets of London, and that Parisians have even seen such a cab at the time of the 1900 exhibition; this simply proves that the thing is possible—which was never placed in doubt—but does not at all prove that it is economical, and this was the only point at issue. Moreover, this special instance was justified by a special reason; the cab was after capital, and was, therefore, playing its legitimate part—plying for hire.

Certainly as much as anyone we are inclined to favour the applications of liquid air, provided they comply with the criterion of being rational, and that they do not involve those who would essay them in fatal miscalculations. This substance has enough strings to its bow to prevent there being any uneasiness as to its future, and it would seem that we should beware at the expense of jeopardising its reputation to pretend that it is a universal provider.

Be it understood, exception must be taken to the pessimistic criticism formulated above, in respect of motive power for certain particular cases where liquid air may present special advantages which assure it a preference. In this way its employment in certain confined localities, mines, submarines, etc., might involve at one and the same time motive power with the cooling and aëration of the

localities in question, and to a certain extent improve their habitability.

We should also except the case where liquid air, in addition to its expansive energy, could also usefully bring into play the chemical energy of the oxygen it contains, as might occur, for example, in feeding the motor of an automobile with superoxygenated air with a view to some sensational feat of speed. To this object compressed oxygen has already been applied, but in such a case we should be rendered impotent by the enormous weight of the metallic recipients which hold it, weighing 10 kgs. per metre cube, whereas the weight of the holders of liquefied gas are by comparison with those of liquid air *nil*.

**Cessation of chemical affinities at low temperatures.—**

We shall see further on subject to priming the reaction, for example, in the case of a burning piece of carbon, liquid air may become the locus *in quo* of chemical phenomena of excessive intensity. But this condition of preliminary priming is absolutely indispensable, because, if bodies be left to themselves at these low temperatures, though they possess the strongest affinities, they may remain indefinitely in contact, without experiencing the slightest modification.

Sodium and sulphuric acid, for example, remain indefinitely side by side in liquid air.

Potassium, which offers one of the most remarkable examples of affinity for oxygen, since it steals it from the hydrogen in water, and at the same time through its combination therewith, notwithstanding the initial achievement, it evolves sufficient heat to spontaneously set fire to the hydrogen thus released—this same potassium can be plunged into liquid oxygen without experiencing the slightest oxidation.

For similar reasons, photographic phenomena are considerably slowed down, at the temperature of liquid air: the interesting experiments of Dewar and the brothers

Lumière have demonstrated this. Dewar, for example, has shown\* that at the temperature of  $-180^{\circ}$  photographic reaction appears to be reduced by 80 per cent.

In one word, the closer we approach to absolute zero, the more the indications of the *death of matter*, foreseen so long ago by physicists, multiply.

Nevertheless, one remarkable exception to the foregoing rule has been pointed out by Moissan, all the more unexpected that it was observed at a temperature far lower than that of liquid air, viz. at  $-250^{\circ}$  C. This consists in the fact that at this temperature the combination of solid fluor with liquid hydrogen takes place spontaneously, and there is no question here of one of those combinations so difficult for chemists, even though fortified with magnifying glasses, to produce after six months' work; the reaction in question is of extreme violence, accompanied by a powerful explosion.

Here we have once more a beautiful theory compromised unless we admit once more that it is the exception which justifies the rule.

\* 'Proceedings of the Royal Institution,' xiv, p. 665.



## CHAPTER X

### CHEMICAL PROPERTIES OF LIQUID OXYGEN

WE have arrived at the capital fact, which dominates the whole history of liquid air and is the basis of the most important of its present applications, that is, the separation of the air into its elements.

This fact, to which we have on many previous occasions already alluded, is that the two elements which constitute liquid air are volatile in different degrees. We shall study further on in detail the peculiarities which arise from this difference. It is sufficient for the moment to recall that on its own initiative when liquid air evaporates, nitrogen, which is more volatile, escapes by preference during the first stages of evaporation, while oxygen is concentrated in the residual liquor to the extent that the latter is finally composed of pure oxygen; this fundamental experiment is carried out in Fig. 102, and you can see that the gas given off at the beginning is chiefly nitrogen as it extinguishes lighted matches—though they be the products of a government monopoly. But the evaporation continues, the liquid becomes richer in oxygen, so, naturally, does the gas which it gives off, and soon, not only is a lighted match not extinguished, but it burns with unaccustomed brilliancy (Fig. 103); finally the residue becomes pure oxygen, a liquid of the density of 1.12, unmistakably blue, strongly magnetic, boiling at  $-182.5^{\circ}\text{C.}$ , and freezing about  $-225^{\circ}\text{C.}$  The yield in oxygen of the progressive evaporation thus carried out is perfectly deplorable; almost all the oxygen is lost in the course of evaporation; it is necessary to reduce the initial

liquid by nine tenths to reach a concentration which permits of satisfactorily succeeding with the experiments indicated above. Suffice it for us to know for the present, that infinitely better results may be obtained by means based upon the *rectification* of liquid air; for the moment we only propose to simply complete our review by enumerating the very interesting properties of this liquid oxygen and the applications to which it can serve as a basis.

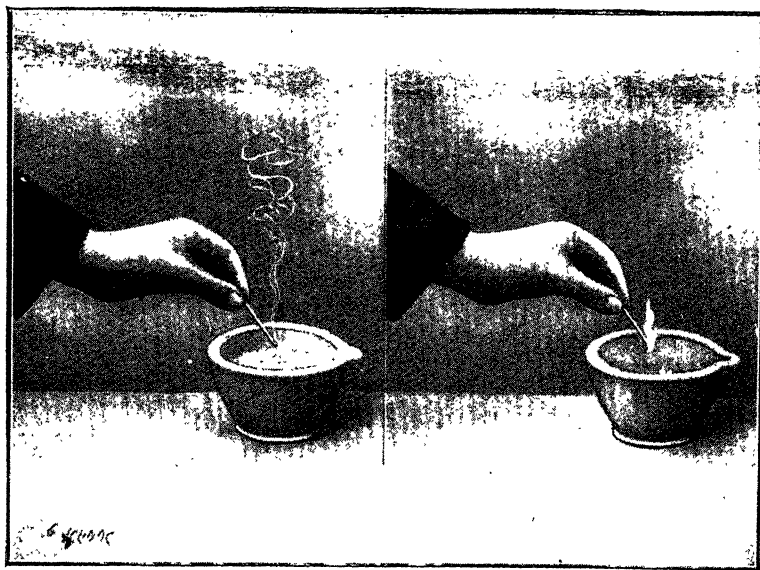
**Vivacity of combustion in liquid oxygen.** — The evaporation which has to furnish us with liquid oxygen, to be sufficiently rapid, may preferentially be effected in a porcelain bowl or dish; double-walled recipients are evidently entirely out of place here. If, when the evaporation is almost over, we introduce in the atmosphere above the bowl a match which has a glowing end, we know that it is set burning again with vivid brilliancy; if the sulphur of the match is not already entirely consumed, it produces at the moment of immersion in the gaseous oxygen a magnificent violet blue flame.

But better still.

If we plunge our incandescent match in the liquid itself, you might expect to see the combustion interrupted, paralysed without recovery, by the intense cold of the liquid. Nothing of the kind! Not only is the combustion continued, but it becomes still more brilliant. We have, therefore, this curious spectacle of a very high temperature in contact with the most fearful cold; this is indeed a case where extremities meet.

Moreover, you may have remarked that it is one of the characteristics of this liquid air, and not one of the least interesting, to allow us to disport ourselves at our pleasure in the most various and the most unlikely spheres of the domain of physical science. We know, for example, with what ease liquid air enables us to realise, thanks to wood

charcoal, the most extreme vacua; while, if we let this liquid air evaporate in closed vessels, we can develop, on the contrary, enormous pressures which may attain 800 atmospheres. On the other hand, liquid air furnishes directly the extraordinary temperature of  $-200^{\circ}\text{C}.$ , whose effects we have learned to appreciate; but if we provoke combustion with its aid we are equally able to reach the



FIGS. 102 and 103.—Extinction followed by lively combustion of a match in evaporating liquid air.

heights of the electric arc in the scale of temperatures: and if, instead of promoting these combustions we care to render them impossible, nitrogen will permit us just as easily to satisfy our desires; these are examples jotted down *currente calamo* which it would not be difficult to multiply.

To return to the preceding experiment, it becomes still more brilliant if we increase the dimensions of the fragment of combustible used. With a piece of charcoal,

or cork, we get veritable fireworks of a very pleasing effect. Fig. 105 illustrates the danger which may accompany such an experiment. We see the extraordinary trajectory which has been described by a fragment of charcoal at the moment of lighting. In these experiments a portion of the gases of combustion, instead of escaping in the gaseous state, are seized by the liquid, which becomes milky through the presence of numerous crystals of carbonic acid.



FIG. 104.—Deflagration of cotton waste dipped in liquid oxygen.

Cotton waste dipped in liquid oxygen and set fire to with a match fixed at the end of a metal or wooden rod deflagrates without exploding, similarly to gun-cotton (Fig. 104). An excess of liquid oxygen is otherwise a drawback to the vivacity of the combustion.

A carbon for an arc lamp heated to redness in a Bunsen burner, then plunged in oxygen contained in a d'Arsonval non-silvered recipient (Fig. 106), continues, of course, burning therein quite tranquilly, with an intense evolution of light and heat, which, as we have seen on

p. 214, can be easily observed externally, so that it is possible to burn oneself when approaching one's hand to this test-beaker full of liquid air.

Iron itself can burn very vividly in liquid oxygen, provided it is plunged therein when heated to a white heat.

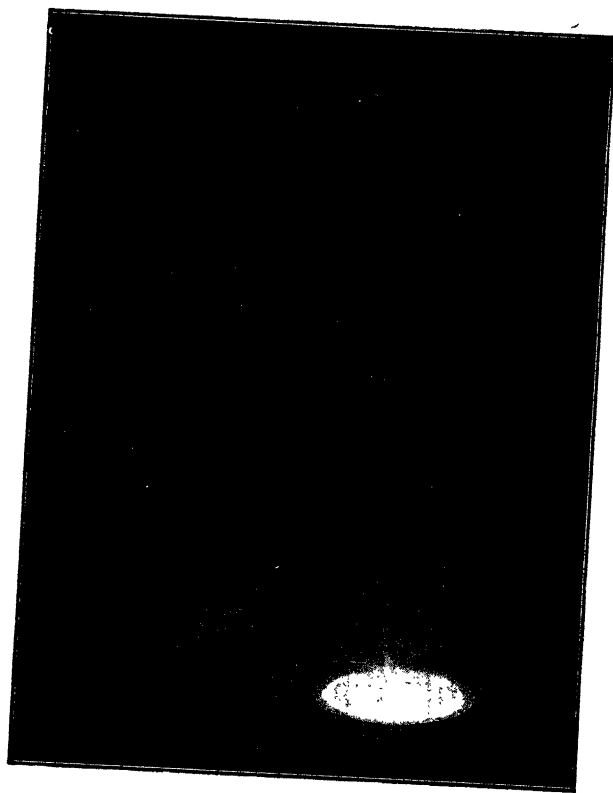


FIG. 105.—Danger of experiments in combustion with liquid oxygen and the precautions they require.

A convenient means for carrying out the experiment consists in suspending by a wire a steel nib at the end of which a small fragment of sulphur is alight, which, when dipped in the oxygen, burns up the steel. The reaction in this case is also very violent and it is preferable to operate in a porcelain vase.

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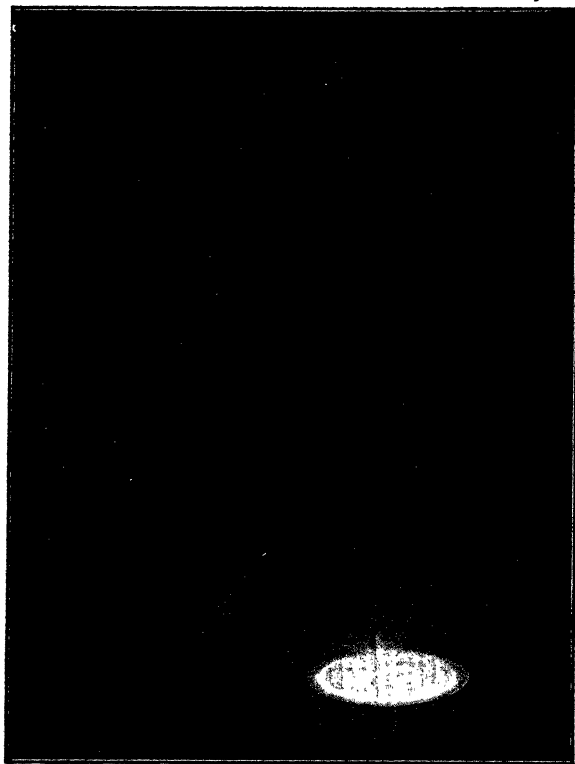


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As to magnesium wire, the orgy of light produced is perfectly overwhelming. A photographic plate cannot cope with it. The last experiment, as well as the preceding, excepting that with an arc lamp carbon, pertain, on the other hand, to a great extent to the following category, and should be carried out with considerable precautions.

**Explosives.**—From these lively combustions we can without effort pass to ultra-rapid reactions, *i. e.* to explosive reactions. It is the possible applications of liquid air to the manufacture of explosives which were the first to attract attention, which is only natural, the sort of spirit of our amiable human nature being what it is.

In carrying out these experiments, it is superfluous to repeat that care must not be relaxed.

Phosphorus offers a first example of this order of facts. A burning fragment of this metalloid let fall into liquid oxygen explodes. The experiment is sufficiently dangerous to not make it recommendable; phosphorus burns are, as is well known, both extremely serious and dangerous. No more should we recommend another experiment of which Claude was on one occasion the involuntary victim, and which it may be said he got out of very well, as he received no greater damage than being enveloped in a cloud of fragments of glass round the least sensitive parts of his face. The experiment consisted in pouring some liquid air, rich in oxygen, close enough to a naked flame to permit of the abundant smoke which is evolved coming in contact therewith; a formidable explosion occurred, causing the breaking of the recipient into a thousand pieces, and setting fire to the alcohol with all the pyrotechnic display of a Brock's benefit. We need not state that in his case the flame did not reach him all alone. But it is well at least that the imprudence of one should benefit others, and if his young comrade, Laborde, a collaborator of Claude's much regretted master, Curie, had read these lines, he might have spared himself



an identical accident, one which was much more serious for him, which was recently spoken of in the papers.\*

Under similar circumstances, that is, in the open air, mixtures of petroleum and liquid oxygen make themselves remarkable by the violence of their explosion. A lighted

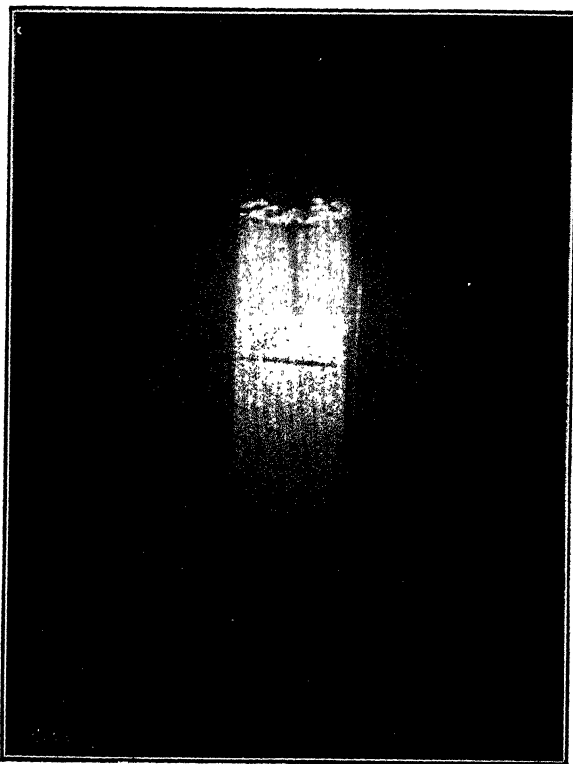


FIG. 106.—Tranquil combustion of an arc lamp carbon in liquid oxygen.

candle falling into a bucket of liquid oxygen sent Claude in 1903 to the hospital in a very pitiable condition.

In this connection a very interesting application of liquid air may be mentioned: pour a little liquid oxygen onto a *small* handful of wood charcoal roughly pulverised and set fire to it; the mixture melts like a mixture of char-

coal and saltpetre, and you obtain in this way a small fire-work, which is almost inoffensive so long as all risk of fire is avoided. But place this mixture in a closed vessel and start the reaction suddenly from a distance, by a capsule of fulminate, for example, and a formidable explosion takes place.

A portion of the Simplon Tunnel was pierced with dynamite of this novel kind.

Among other advantages, this new explosive presents that of being less expensive than dynamite, because beyond the charcoal and the labour and the cost of writing off the appliances, it only costs some power, to wit about 2 H.P. hours per kilogramme of liquid oxygen, which is very little in localities where power is cheap. There is in addition the evaporation of the liquid air between the instant when the cartridges are set and that when they are exploded which may cause some miscalculations. This fault is inevitable, but it may be valuable, seeing that the use of cartridges of this kind would do away with the serious danger of belated explosions, which are often the occasion, with explosives in common use, of a misfired shot, for cartridges whose basis is liquid oxygen evidently become wholly inoffensive in a few instants.

We have taken up recently in this connection some very encouraging experiments, of which it is still a little early to give the details. What we can say on the subject at present is that it is our firm opinion that the manufacture of explosives will certainly have some day to take into account this rather unexpected application of liquid oxygen.

Similarly wool and cotton, which, dipped in liquid oxygen, catch fire and burn in the open air, deflagrating in the same fashion as gun-cotton (Fig. 104), produce an explosion if they are set fire to in a closed vessel by a capsule of fulminate.

**Transformation of oxygen into ozone at low temperatures.**—Finally, it is interesting to point out that liquid oxygen and gaseous oxygen at low temperatures are easily transformed by efflux into ozone, which condenses into a dark indigo blue liquid which is readily explosable. The yield of the ozonisation thus brought about is considerably better than at ordinary temperatures, and it is certain that this fact will be invaluable in the industrial production of bodies capable of violent affinities and in many different applications.

## PART IV

# THE SEPARATION OF THE AIR INTO ITS ELEMENTS

### CHAPTER XI

#### GENERAL CONSIDERATIONS; DIVERSE PROCESSES

**Importance of the problem.**—Of all the problems which at the present time call for human ingenuity, there is, doubtless, none of more importance than that of the manufacture, at very low cost, of oxygen, seeing that this gas is the source of all life and all combustion on the surface of the globe, that hundreds of reactions used in the most important manufactures equally depend thereon, and that all this can be intensified, vivified and amplified, in any measure we may desire, by the substitution of, more or less, pure oxygen for air.

The list of the applications which, in this connection, might be compiled is endless, and what proves that such a list would still be incomplete, and shows how many would be the surprises which we might reasonably expect, is that among present uses of commercial oxygen two of the most interesting are closely connected with applications which it would have been truly difficult to foresee—the cutting of metals with oxygen, and the manufacture of artificial precious stones.

As, to nitrogen, if it does not possess as many cords to its bow, it has one which is indubitably its very own, and which enables it to dispense with all else; it is the essential basis of manures—that is, of a business which, though still in its infancy, attains already a yearly turnover of more than 500 million francs (£20,000,000).

Hence the unparalleled ardour with which we are perfecting at the present time the processes of manufacture of nitric acid by electrolysing the air, of fixing atmospheric nitrogen under the form of ammonia, of cyanides, of cyanamide, etc., which undoubtedly constitute one of the biggest industrial questions now on the tapis, and in which the influence of the processes of which we are going to speak will be decisive.

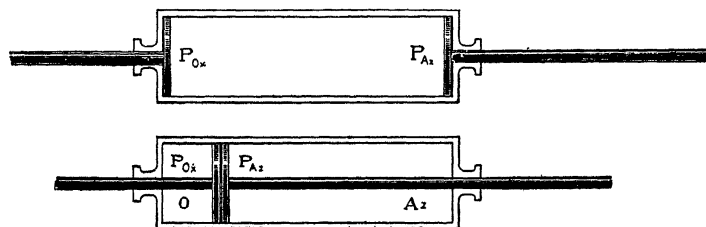
The space here is too limited to review all the possible or probable successful applications of oxygen and nitrogen, and we are obliged to make them the subject of a separate work.

To only speak of oxygen, the choice of the raw material from which to obtain it, would be very complicated if we had to review the very numerous sources of oxygen which nature offers us. But of all these sources, the two by far the most interesting, both because of the universality of their presence on the surface of the globe, as well as of their facility of access to appliances for their use, are assuredly *air* and *water*, and it is only between these two raw materials that we need exercise our choice.

Now, a crucial argument, an argument of a kind to do away with all hesitation may be advanced in favour of atmospheric air. In water, moreover, the two elements, hydrogen and oxygen, are combined with extreme energy. Certainly, by its marvellous power, electricity is able to undo these bonds and liberate this oxygen and this nitrogen; but it necessarily requires the expenditure of a considerable quantity of energy to do this.

On the contrary, air is a simple mixture; no affinity binds the oxygen molecules to those of nitrogen, and consequently a small amount of energy—at least theoretically—is required to separate them.

**The separation of the elements of the air requires energy.**—We must not, however, fall into a very prevalent error. It is a generally received axiom among engineers that the separation of two gases without chemical affinity theoretically *costs no energy*. Now it is nothing of the sort; as we have just stated, it costs in reality very little energy—but not none at all. To demonstrate this, and at the same time calculate the value of the work theoretically necessary, we shall use a very elegant and very simple



Figs. 107 and 108.—Demonstration of the necessity for an expenditure of energy to separate the air into its elements.

proof, the elements of which were suggested to Claude by Professor Ostwald on the occasion of a visit he paid to the works of the Claude Company.\*

Let us imagine that the air to be separated, considered, to simplify matters, as consisting one fifth of oxygen and four fifths of nitrogen, is placed (Fig. 107) in a closed cylinder.

Suppose also that at the two extremities of this cylinder there are two pistons which can move towards each other, but which present the peculiarity that one,  $P_{O_2}$  is perfectly *perméable* to oxygen, but *impermeable* to nitrogen, while the other,  $P_{A_2}$ , is permeable to nitrogen only.

\* The first idea of this demonstration is to be found in a work by Van der Waals.

The idea of these semi-permeable walls has nothing irrational about it, because such walls might be made up by a layer of liquid dissolving the one but not the other of the gases, and on the other hand, the diffusing walls which allow the different gases to pass with unequal velocities are already a first approximation thereto.

Let us advance the piston  $A_z$  to the left by four fifths of the length of the cylinder (Fig. 108). Being permeable for nitrogen it does not experience any resistance through the presence of the nitrogen: its only obstacle arises through the compression of the oxygen which it has to drive in front of it, and which it brings in this way from its initial partial pressure of one fifth of an atmosphere to a final effective pressure, if the compression be supposed to be completed isothermically, exactly equal to 1 atmosphere.

The work thus expended by  $P_{Az}$  is therefore equivalent to the work of compression of the oxygen from its partial pressure of one fifth to that of 1 atmosphere.

Let us pass now to the piston  $P_{Ox}$ , and let us advance it towards the right by one fifth of the length of the cylinder, that is, till it comes in contact with  $P_{Az}$ . We see in the same way that this piston, while experiencing no resistance to its motion because of the oxygen, by which it is permeable, has still to overcome the resistance to compression of the nitrogen which is propelled in front of it (across  $P_{Az}$ , which is transparent for this nitrogen), and brought from its initial partial pressure of four fifths to the final pressure of 1, A. When this second manœuvre is accomplished, all the oxygen of the mixture is behind  $P_{Ox}$  at atmospheric pressure, all the nitrogen is behind  $P_{Az}$  also at atmospheric pressure, and the air is separated into its elements. But we have seen that to achieve this has cost something: it has cost a total work equal to the sum of the separate work of isothermic compression of each of the gases, from its partial pressure in

the mixture up to its total pressure—a remarkable statement of a law which should be known, and become classical on the same footing as Dalton's law of partial pressures, of which it is a consequence.

The expenditure of energy thus determined for this separation, is certainly the smallest which it is possible to incur to realise same, because it has been obtained in an operation which is obviously reversible and perfect—that is, accomplished without useless expenditure of energy.

We have just said that the operation is reversible. If, in effect, the gases being separated, we leave the pistons free to act of themselves, they will return to their respective positions by the action of the pressure of the nitrogen on  $P_{Ox}$  and of the pressure of the oxygen on  $P_{Az}$ ; and they will be able to effect, with the absorption of the equivalent heat, work equal to the sum of their several work of expansion from 1 atmosphere down to their respective partial pressures—a work produced precisely equal to that absorbed in the inverse operation.\*

It is curious to observe that between the mixture of these gases thus effected in a reversible way, and the irreversible mixture by simple addition, the same difference exists as between expansion with external work which produces mechanical work, and expansion without external work, which is, so to speak, sterile so long as the internal work is negligible.

The theoretical work of separation, calculated according to the above conditions, corresponds very closely to *one*

\* The possibility of obtaining mechanical work through the simple mixture of two gases without mutual affinity has been demonstrated in 1875 by Lord Rayleigh ('Philosophical Magazine,' xlix, p. 311). We can see according to this how faulty is the argument which, to support the thesis of the non-existence of the work of separation, simply states that the mixture of two gases without affinity neither produces nor absorbs heat. This is only true—so far as internal work—when the mixture is effected in the habitual way by the simple addition of the two gases one to the other, which is an essentially irreversible process; but when, on the contrary, it is effected as above by a reversible process, we have just seen that it implies a quite appreciable absorption of heat.



*tenth of a h.p. hour per cubic metre of oxygen separated.* The practical processes will approach all the closer to this result the nearer they are to a reversible process; but, as we have already had occasion to observe (p. 96), this work is already too considerable to be within the capacity of a simple fan, and this fact appears to us to furnish the reason for set-backs which have been experienced up till now in the question of the separation of gaseous mixtures by centrifugal action.

In any case there is long interval between the theoretical limit which we have just determined and that, equally theoretical, which corresponds to the case of the electrolysis of water, which calls for no less than *nine h.p. hours per cubic metre of oxygen*. If the theoretical superiority of air in this respect is not indefinite, as those suppose who fall into the error indicated above, it remains nevertheless a very respectable one. We have therefore decidedly no hesitation in choosing the raw material, and it is to air that we have to look: all the more so that if with air we lose the bye-product *hydrogen*, we gain in its place *nitrogen*, whose uses, as we have pointed out, promise to become gigantic. The source of oxygen on which we shall draw, in the future is, therefore, the atmosphere, an unequalled source which, if it were condensed, would cover our globe with a liquid ocean whose depth would not be less than 13 times the height of the barometric column, say about 10 metres, of which 8 would be nitrogen and 2 oxygen. This corresponds to not less than 1300 cubic metres of gaseous oxygen per square metre of the surface of the earth. If we consider, on the other hand, that the total surface of globe equals  $5 \times 10^{14}$  (about) square metres, and as the number of human beings is about 1,000,000 millions, the proportion of oxygen allocated to each human unit—that is, the proportion of which a manufacturer of oxygen could legitimately dispose, on the supposition that

he has not the right to touch the share of others, will still amount to the very respectable figure of

$$1300 \times \frac{5 \times 10^{14}}{109} = 650 \text{ million cubic metres!}$$

Let us add further that among all the bodies spread over the surface of the globe, the air is the only one which under all circumstances of time and place may be considered as wholly free. Water is not found everywhere; considerable expense is often necessary to obtain it, whether we have to seek it at considerable depths, or we have to lay hands on it at a considerable distance. The earth itself makes it necessary for us to extract it at the price of considerable labour and lead it to where it is to be utilised. The air exists on every side, and as an ideal raw material it delivers itself into the apparatus where it is to be used, however large the consumption may be.

**Various processes for the extraction of oxygen from the air.**—This superiority of air over every other source of oxygen was clearly apparent to a number of investigators, of which the first in point of date was doubtless that genial forerunner, Tessié du Motay. Being persuaded of the immense advantage which the production of oxygen at a very low price would present, Tessié du Motay invented as far back as 1867 a remarkable process based on the absorption of oxygen in the air by *manganate of potash*, and the regeneration of this manganate by a current of water vapour which should set at liberty the oxygen thus absorbed. It was with this process that Tessié du Motay succeeded in producing the oxygen for some very interesting experiments, and particularly for the lighting of the square of the Hotel-de-Ville in Paris with the Drumond light. Saint-Claire Deville and Debray, on their side, have used *sulphuric acid* as their raw material, the whole of whose oxygen was, in point of fact, obtained from the atmosphere. They caused this acid to fall drop by drop into an earthen-

ware, funnel filled with fragments of porcelain and heated to an incipient red: the acid decomposed thereupon into oxygen, water and sulphurous acid, which was absorbed in an alkaline solution.

Mallet has proposed to absorb the oxygen in *perchloride of copper*, which is then transformed into *oxychloride*, which, heated to 400° C., regenerates the perchloride by giving up the oxygen absorbed. Finally, Boussingault has indicated a process which, perfected and rendered practical by various inventors, and specially Messrs. Brin, has attained a commercial development of considerable importance. This process consists in absorbing the oxygen of the air by *baryta*, heated to a dark red, and by causing this oxygen to be given up either by raising the temperature, or, preferably, by the action of a suitable vacuum. The absorption of the oxygen may, on the other hand, be hastened by delivering compressed air in retorts under several atmospheres' pressure. Baryta loses little by little its absorbent qualities and has to be replaced after a certain number of operations.

Besides this, the oxygen thus obtained holds pretty often traces of carbonic oxide, which passes through the walls heated to redness of the cast iron retorts, and which might present some drawbacks if the oxygen is intended for medical use.

Each of these processes is certainly not by a long way of sufficient importance to vie with the great output of processes based upon liquefaction of the air, to the study of which we will now pass without further to-do.

he has not the right to touch the share of others, will still amount to the very respectable figure of

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## CHAPTER XII

### PARTICULARS OF THE EVAPORATION OF LIQUID AIR

**Parkinson's idea.**—The basis of the separation of the elements of the air by the method of liquefaction is, as is well understood, the difference in their volatility.

Whereas oxygen boils under atmospheric pressure at  $-182.5^{\circ}$  C. (Travers), nitrogen only boils at  $-195.5^{\circ}$  C. Boiling at the lower temperature, nitrogen is more volatile than oxygen, similarly to alcohol, which boils at  $+79^{\circ}$  C., is more volatile than water, which boils at  $100^{\circ}$  C. Hence the consequence, already known to us, and pointed out for the first time by Dewar, that when liquid air boils, the nitrogen, which is more volatile, is preferentially given off during the first portion of the evaporation, while the residual liquid becomes progressively richer, up to the limit where it is finally composed of pure oxygen.

At first sight the difference of  $13^{\circ}$  C. which separates the respective points of ebullition of oxygen and nitrogen might appear a small matter. But we ought here to recall the fact that at the abnormal temperatures at which we are working, the nearness of absolute zero bestows on each degree, an enormous importance. In reality, our  $13^{\circ}$  C. are equivalent to a difference of  $60^{\circ}$  reckoned at the temperature of boiling alcohol. Now the difference between alcohol and water being only  $21^{\circ}$  C. instead of  $60^{\circ}$  C., we arrive at this conclusion, somewhat paradoxical at first blush, but further strengthened by the absence of all affinity between oxygen and nitrogen, that the separation

by distillation of these two elements must be far easier than that of alcohol and water!

Here we have a first process for the manufacture of oxygen. We can evaporate liquid air, and collect separately the final portions of the evaporation. If, as we have stated above, the scientific ownership of this observation belongs to Dewar, the daring thought of utilising this fact commercially for the production of oxygen and nitrogen must be attributed to Parkinson: it was put forward in an interesting patent\* worked out as far back as 1892, to the consideration of which we shall recur later.

And in this connection we wish to clearly indicate what wonderful intuition Parkinson must have at that time possessed, to have entered upon such a course. We must not forget that liquid air was then only an extremely rare curiosity. Even now, moreover, liquid air costs relatively much, because it is obtained by great expenditure of power, at the rate at most, of a litre per H.P. hour. Now even supposing that the process was carried out in accordance with the seductive formula of certain inventors who are the friends of simplicity: we evaporate four fifths of the liquid air; the nitrogen disappears, the oxygen remains—one operation, that is all. We shall see in an instant how much we must discount of this beautiful programme; but even if it were possible to realise it, 230 grm. of oxygen per kilogramme of liquid air, that is, 150 litres per H.P. hour, appear to us to be the extreme limit of permissible ambition, since it would hardly seem possible, you will agree, to obtain from liquid air more than the 230 grm. per kilogramme which it contains.

This is, you see, by no means a very brilliant result.

And if, on the other hand, we hark back to realities, how much less encouraging still are the determinations which we have yet to make!

**Peculiarities of the evaporation of liquid air.**—When liquid air evaporates, in point of fact, it by no means does so with the seductive simplicity which we have been considering. Even at the very commencement of evaporation the nitrogen given off is not pure nitrogen. It carries with it 7 per cent. of oxygen. If the loss of oxygen were continued only at this rate, it would suffice to limit the yield of the operation to two thirds. But, be it understood,

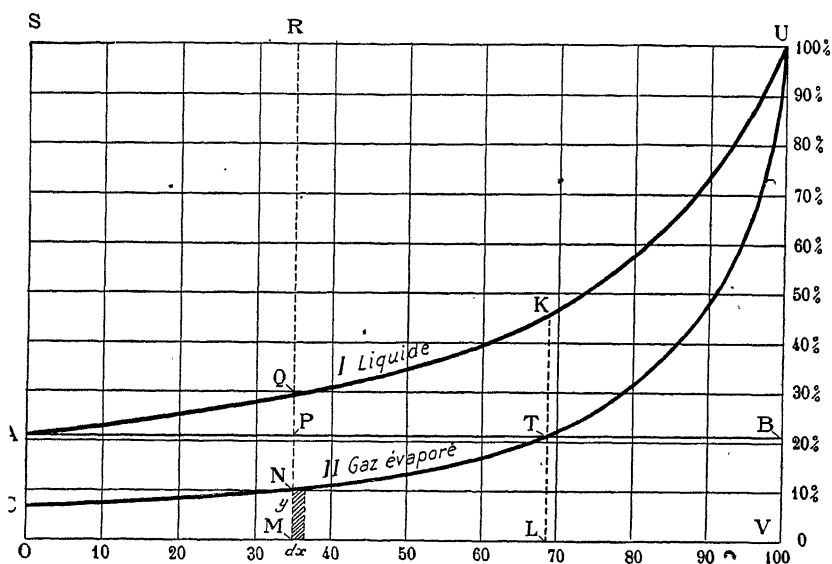


FIG. 109.—Evaporation of liquid air according to Linde.

matters would rapidly get worse in the course of the operation. The temperature of liquid air, which at starting was close to that of liquid nitrogen, viz.  $-193.5^{\circ}\text{C}$ ., and which in itself was sufficient to cause in the oxygen a serious vapour tension—whence the initial 7 per cent. loss—rises progressively as the oxygen becomes richer, to end inevitably at  $-182.5^{\circ}\text{C}$ ., the temperature of ebullition of pure oxygen. As a consequence, the partial tension of the oxygen increases little by little, so that as the liquid becomes



Instead of being concentrated exclusively in the residual liquid, the oxygen diffuses itself outside thereof in a lamentable fashion during the whole course of evaporation in an increasing proportion the greater the degree of purity aimed at. To calculate this loss let us represent by curves the above results. These curves, are shown in the form determined by Professor Linde in Fig. 109.

Curve I indicates the richness of oxygen in the "liquid phase" as a function of the evaporation; curve II gives the corresponding richness of the "gaseous phase"; the degrees of evaporation are taken as abscissæ, and these abscissæ have the peculiarity of being in relation to the evaporation of 100 parts normal liquid air, that is, of the test of 21 per cent. counted volumetrically in the gaseous state. We see that, according to what we already know, the test in oxygen of the evaporated gas is constantly lower than that of the liquid from which it is derived; this test of the gas rises, however, more and more rapidly, so that from 7 per cent., the initial value, it reaches 100 per cent. when the liquid which is evaporated is reduced to its last drop.

Now let  $dx$  be an elementary evaporation at the point  $m$ , and let  $y$  be the ordinate corresponding to  $MN$  of curve II. The quantity of oxygen carried over in this evaporation  $dx$  is measured by the small surface  $ydx$ . The surface  $cnmo$  of curve II up to  $m$ , which is  $\int ydx$ , therefore represents the total quantity of oxygen lost in the evaporation  $om$ . As  $NR$  manifestly indicates the test of the gases in nitrogen at the point  $m$ , we shall see in an analogous way that the surface  $suvo$  represents the total initial liquid, each of the 100 parts of this liquid being represented by one of the 100 small squares of the figure; the portion of  $suvo$  to the right of  $MR$  represents the non-evaporated liquid, and that to the left the evaporated liquid of which  $cnmo$  is the oxygen

Thus CNMO represents the loss of oxygen incurred to reach the point M of the evaporation. It is now easy to follow the progress of this loss, all the more so as we have already remarked each little square in the figure represents one hundredth of the air operated on.

For example, we see very easily that up to the evaporation 50 the loss of oxygen equals the surface of 5 small squares with respect to 50. The average test of the evaporated air up to this point is therefore—

$$\frac{5}{50} = 10 \text{ per cent.},$$

and the test of the gas resulting from the *total* evaporation of the liquid remainder will be—

$$\frac{21-5}{50} = 32 \text{ per cent.}$$

We also see that the evaporated air at T reaches the test of ordinary air, that is, 21 per cent., when the 100 parts of the initial liquid are reduced to 31. The surface below curve I up to this point, 31, indicates for us that up to that point 7 parts of oxygen have been lost, accompanied by  $69-7=62$  parts of nitrogen. These 7 parts of oxygen are evidently lost to us, because there is naturally no interest from the point of view of the oxygen to recuperate gases less rich than air. But starting from this point, there may be interest to do so, and if we recuperate then up to the end, the composition of the mixture obtained will be manifestly given either by the average ordinate of curve II starting from T, or about 47 per cent., or directly by the test  $KL=47$  per cent. of the residual liquid.\* In this case the loss, therefore, is limited at that point to the 7 parts of oxygen lost, so that we can recuperate, in the form of a mixture

\* It is, in fact, an obvious general property of curve I that its ordinate QM at point M is necessarily equal to the average ordinate of curve II starting from point T.

testing 47 per cent.,  $21 - 7 = 14$  parts of oxygen—that is, about two thirds of the oxygen in question.

The result would therefore be relatively favourable if we could rest contented with a degree of purity of 47 per cent. But this is not often the case, and we shall see with what rapidity the yield diminishes when we attempt to go further.

Suppose we desire to obtain an average gas testing 60 per cent. With this object it is necessary to push the evaporation very far and only to commence collecting at the point where the liquid tests 60 per cent. The curve shows us that to do this we must evaporate 82 parts of the liquid before beginning to collect the gases, which at this moment test 33 per cent. The quantity of gas collected is therefore  $100 - 82 = 18$  parts testing 60 per cent., which is in oxygen  $18 \times 0.6 = 10.8$  parts in 21. The yield is now only 50 per cent. It falls to 15 per cent. if we wish to collect the oxygen under the very moderate oxygen test of 90 per cent.! This reduces to 20 litres—and no longer 150—the quantity of oxygen obtained per kilogramme of liquid air, and the cubic metre now costs 50 H.P. hours—three times dearer than by the method of electrolysis of water!

We see what disillusion awaits our simplicist inventors of a few lines back should they ever dare to pass from “theory” to practice.

**Baly's experiments.**—Before proceeding further, we should state that Baly, Sir W. Ramsay's assistant, has undertaken, on his side, analogous experiments to those of Linde, but extended to all the mixtures which can be formed, not only starting with liquid air, that is, from the test of 21 per cent., but from zero, that is, from pure nitrogen. These experiments give at one and the same time the temperatures of the liquid as a function of its composition. We give in the following table the results, to which we shall have very often to refer in what follows.

Test of the liquid phase.	Test of the gaseous phase.	Corresponding temperature. °C.	Test of the liquid phase.	Test of the gaseous phase.	Corresponding temperature. °C.
0°00	0°00	-195·46	69·31	40·45	-188·5
8°10	2°18	-195°0	72°27	44°25	-188°0
15°25	4°38	-194°5	75°10	48°17	-187°5
21°60	6°80	-194°0	77°80	52°19	-187°0
27°67	9°33	-193°5	80°44	56°30	-186°5
33°35	12°00	-193°0	82°95	60°53	-186°0
38°53	14°78	-192°5	85°31	64°85	-185°5
43°38	17°66	-192°0	87°60	69°58	-185°0
47°92	21°22	-191°5	89°82	74°37	-184°5
52°17	23°60	-191°0	91°98	79°45	-184°0
55°94	26°73	-190°5	94°09	84°55	-183°5
59°55	29°93	-190°0	96°15	89°80	-183°0
62°92	33°35	-189°5	98°16	95°10	-182°5
66°20	36°86	-189°0	100°00	100°00	-182°0

Baly found that these results can be represented with remarkable exactitude by the equation :

$$\log r' = a + b \log r,$$

in which  $r$  is the ratio of the two elements in the liquid and  $r'$  that in the gas.

Subjoined is the degree of concordance furnished by the calculated and observed values of the ratio of oxygen to nitrogen in the gaseous phase.

Temperature. °C.	$r'$ observed.	$r'$ calculated.
-193	0·136	0·137
-191	0·309	0·310
-189	0·584	0·586
-187	1·090	1·090
-185	2·290	2·300
-183	8·810	8·870

For facility of comparison we shall place Baly's results in the form shown in Fig. 110; the tests of the liquid phase are written as abscissæ, those of the gaseous phase as ordinates. In addition curve II indicates the variation in temperature of the liquid progressively with the

concentration in oxygen, a rise which follows naturally the progress of this enrichment, and which, like it, is slow at starting, and progressively accelerates.

We have already mentioned this rise of temperature in the liquid air as a function of its evaporation, but it is well

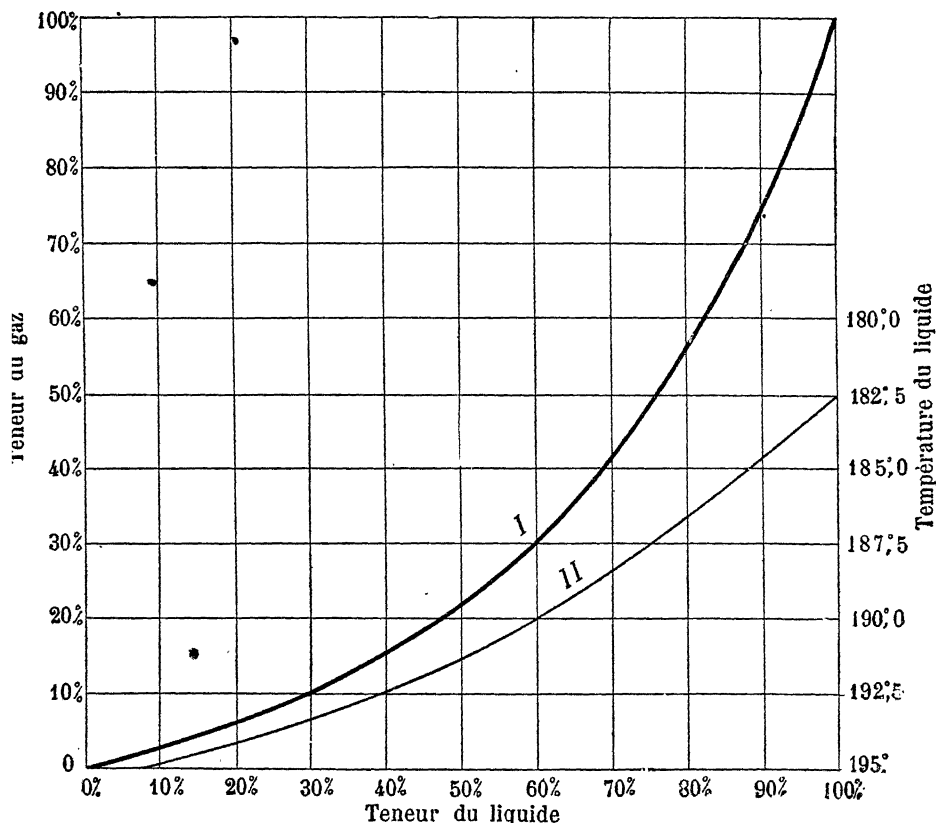


FIG. 110.—Respective tests of the liquid and gaseous phases and temperatures of the liquid air as a function of its composition according to Baly.

to insist thereon, because the fact that liquid air is proportionately less cold the richer it is in oxygen is the capital fact on which all the rest depends, not only from the point of view of evaporation, but equally, as we shall see, from the point of view of the peculiarities of progressive liquefaction and of rectification.

## CHAPTER XIII

### THE RECUPERATION OF COLD

EXCEPTING the case where one can content oneself with only slightly enriched air, we now know that the spontaneous evaporation of liquid air is a very deceptive operation in respect of yield. This defect seems to be irremediable and the method seems doomed to a very precarious existence, since our meagre theoretical yield of 150 litres of oxygen per H.P. hour cannot in practice be approached by a long way.

To change all this, a very simple idea has sufficed. Up to the present we have evaporated our liquid air as we evaporate water or alcohol. At most, instead of placing this liquid air on a source of heat, we have made use of the free heat of the atmosphere, which, as we already know (p. 208), is amply sufficient: this is already an appreciable advance, since evaporation thus produced *costs nothing*. But, whether it be by means of a source of heat or by the free heat of the air, the evaporation of liquid air in such a fashion, amounts to using up without profit to anyone, its very costly cold, its cold which we had such difficulty in producing by the help of expansion.

Now, there is much better to be done. Instead of destroying this cold, we should *recuperate* it.

This is Parkinson's excellent idea: the result has demonstrated all its resources, and it dominates to-day by its economical possibilities the whole of the industry we are considering.

We are compelled, therefore, to return to Parkinson's

patent, and examine in what way this primordial question of recuperation is treated therein. But in this remarkable patent the ideas are numerous, and here is what we have found to glean from a preliminary sentence: "Nitrogen may be separated from oxygen by slightly heating the recipient which holds them, for example, by means of a current of atmospheric air; nitrogen, which has its boiling-point lower than oxygen, evaporates and leaves the oxygen."

Doubtless, Parkinson is possessed here with the idea, which is reasonably simple, of an integral separation: but it is none the less true that here the principle of the industrial utilisation of liquid air for the manufacture of oxygen, and in addition, the means universally used ever since of borrowing the heat required for evaporation from the atmospheric air, are formulated.

Now these are the special terms in which the idea of recuperation is indicated.

"To make the process economical, the air to be treated should be cooled as much as possible before entering the worm where it is liquefied. Through the cooling of the air at the expense of the oxygen and the nitrogen which are separated, we can bring about the separation of the atmospheric air in a continuous, rapid and economical way."

We see not only that Parkinson indicates a means of recuperating the cold—a means destined to be used universally after him, consisting in fixing the cold of the separated gases in the air to be liquefied—but also, he underlines the economical signification of this recuperation; the costly element in the operation is the cold of the liquid air at stake; therefore, not only must we recuperate this cold, but recuperate it as efficiently as possible.

Now on this theme what says theory?

**Concomitant evaporation and liquefaction.**—We know that to evaporate liquid air it is necessary to impart heat

thereto ; we know also that the quantity to impart for this object, which is an exact measure of the latent heat of evaporation, is 48 therms per kilogramme for the nitrogen and 51 for the oxygen, and, *grosso modo*, 50 for the liquid air.

But this only represents the heat absorbed by the change in physical state through the passage from the liquid to the gaseous state ; after this absorption our kilogramme of liquid air, separated, moreover, through the evaporation itself into its elements, is transformed into 1 kg. of gas at the average temperature of  $-190^{\circ}\text{C}$ . It still retains, therefore, by reason of its temperature, and by comparison with the temperature of the environment, a quantity of cold equal to the product of its specific heat, 0.24, into the difference of temperature, about  $200^{\circ}\text{C}$ ., or an amount of about 50 therms. In other words, to each kilogramme of liquid air we must impart 50 therms to evaporate, and other 50 to heat up its elements to the temperature of the environment.

Let us now take 1 kg. of air from the atmosphere and set out to bring it to the liquid state, no longer by violent compression and expansion, as in the liquid air machines, but by the simple subtraction of heat. The operation is manifestly the inverse of the preceding ; we must take away from this kilogramme of air firstly its heat of refrigeration, to wit 50 therms, whose removal will bring it, still in a gaseous state, to  $-190^{\circ}\text{C}$ ., and then take away from it its heat of liquefaction—that is, another 50 therms—whose removal will then bring it to the liquid state.

Therefore—and we must be excused for insisting upon such elementary considerations, because these abnormal temperatures have a trick of arousing doubts in the mind in connection with the simplest things—therefore, we say, to evaporate and then to be heated up, 1 kg. of liquid air requires a quantity of heat precisely equal, and precisely of



the same quality, as that rendered available by the refrigeration followed by the liquefaction of 1 kg. of the surrounding air.

Let us find a method of making the two operations concomitant, and each time we evaporate a certain quantity of liquid air, each time that we separate the oxygen from the nitrogen by this fact, we *reconstitute* a quantity of liquid air *precisely equal* to that which we have evaporated!\*

In this conception the recuperation is complete, the expenditure of liquid air is *nil*, and the separation of the elements of the air appears to be gratis!

Here evidently is a consequence of the fact that the air being constituted by a simple physical mixture, through the simple gaseous diffusion of two gases without reciprocal chemical affinity, these two elements are inclined to allow themselves to be separated without opposing much resistance. We have seen, however (p. 292), that this separation, even theoretically, calls for a certain expenditure of energy; the above conception cannot therefore be entirely correct, and we shall effectively be led to applying certain restrictions thereto.

To resume, we have to recuperate (*a*) the cold brought into operation by the evaporation of the liquid air; (*b*) the cold of the evaporated gases between their initial temperature and that of the environment.

Let us return to Parkinson's patent; we have seen that the second portion (*b*) of this programme is realised by him in a perfect fashion by means of exchangers of temperature. We are now going to see in what a somewhat singular way

\* Let us remark that this, however surprising it may appear at first blush, is simply identical to what is produced in steam evaporation when this steam is condensed to an amount precisely equivalent to the water evaporated; so that if water were a precious liquid through its possession of the liquid form itself, and if its steam, on the contrary, cost nothing—which is precisely the case with liquid air—this method of evaporation would be incomparably superior to evaporation in an open vessel, since the supposedly precious liquid would be continually reconstituted. Now this is exactly what Parkinson's patent achieves.

he treats the first portion (*a*) itself. What, in point of fact, does the inventor do with the air to be treated, after having cooled it and recuperated the cold of the oxygen and that of the nitrogen in the exchangers? He proceeds to liquefy it, as his object is ultimately to evaporate it, and to separate

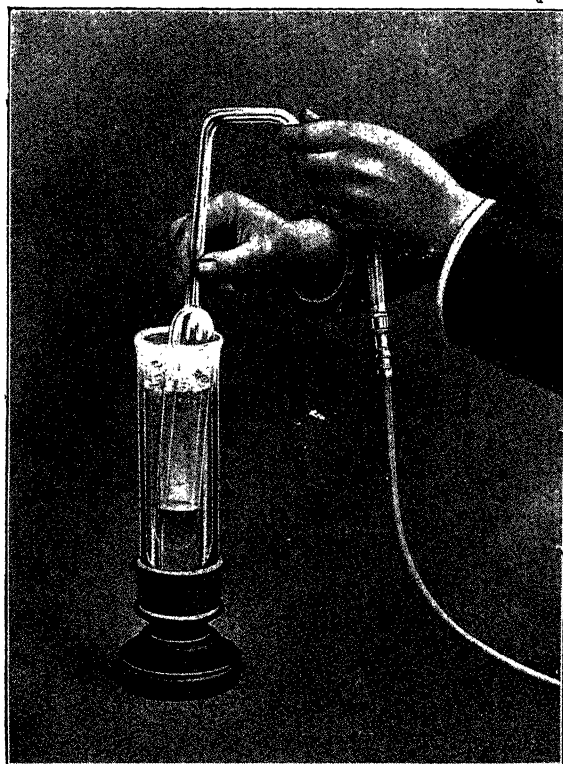


Fig. 111.—Experiment on the ready liquefaction of atmospheric air in liquid air.

elements. He sends it with this object through a tubular system submerged in the *auxiliary* liquid air, and he specially observes that to enable liquefaction to supervene *slight excess of pressure* in the air to be treated, such as can be furnished by a fan, is in this case sufficient.

To show how well founded this idea is, and with what

ease, with what facility this liquefaction of air, under such conditions is effected, we are going to repeat the experiment (Fig. 111) by pumping air with a small bicycle pump into this glass globe immersed in liquid air. We can see the globe progressively filling with a whitish liquid which is nothing more nor less than liquid air holding in suspension carbonic acid ice.

Let us continue the experiment and direct our attention to another of its peculiarities. The liquefaction thus realised is manifestly the reverse of an evaporation; for this evaporation, as we know, *absorbs* heat, while liquefaction *gives it off* in a sensibly equal amount (p. 20), and you can see that the heat given off by the liquefaction of the air in the goblet is effectively represented by the *violent ebullition* of the external liquid, which is progressively evaporated.

Parkinson's idea is therefore justified, and the desired evaporation is realised. In this evaporation the separative action elucidated by the author is produced, the nitrogen evaporating first and the oxygen next. Therefore in conformity with his object, which was to obtain oxygen, and in conformity with the ideas on recuperation which he expressed in luminous fashion in the lines cited above, Parkinson is going to separately collect this oxygen and this nitrogen, after having caused them to pass through his exchangers in the opposite direction to the compressed air to collect their cold—and these problems will in this way have been solved in a marvellous fashion ever since 1892.

Well, nothing of the kind!

Through an astonishing forgetfulness which exceeded the limits of the most colossal absurdities of the ever absent-minded scientists, and which clearly shows the somewhat speculative side of the ideas he had expressed, Parkinson forgot at one and the same time the object he had in view and the essential principles he had just formulated.

The marvellous task he had just achieved had been

## 12 SEPARATION OF THE AIR INTO ITS ELEMENTS

he oxygen and nitrogen which he has just produced, which are the very objects of his efforts, he allows to escape without thinking of collecting them, and not only does he not collect them, but he allows them to escape with all the cold whose recuperation an instant ago he had so convincingly advocated.

And it is only liquid air that he thus actually prepares, evaporated by a barbarous method with the aid of gaseous

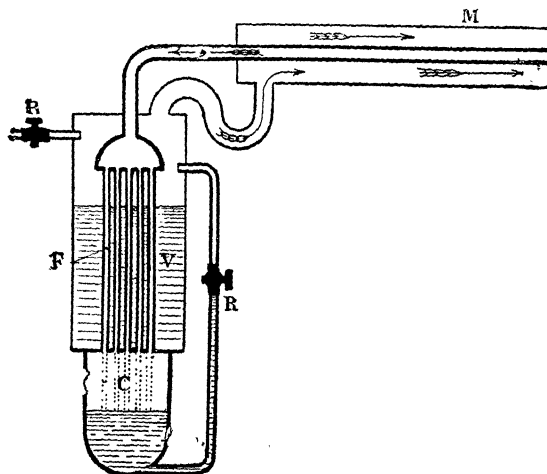


FIG. 112.

circulating around it, of which he ultimately decides to let the elements after having collected their cold !

The inconsistency is manifest, and astonishment apart, reader, guided by the explanations of Parkinson himself, have no difficulty in appreciating it.

We have now in hand all the elements to definitely construct a rational system of progressive evaporation for air with recuperation of the cold.

To realise in practice our conception, we are, in fact, led to the following device (Fig. 112).

The liquid air to be evaporated is placed in a boiler *v*, a bundle of tubes *f* being immersed therein ; the atmospheric

air destined to provide by its liquefaction the heat required for evaporation, reaches this system of tubes after passing through the exchanger *m* in the contrary direction to the evaporated gases. In the exchanger it is cooled down to about  $-180^{\circ}\text{C}$ ., retaining the cold of an equal weight of evaporated air; in the system of tubes it is liquefied while bringing about the evaporation of an equal weight of external liquid.

**Necessity for compressing the air to be treated.**—Nevertheless, an important reflection occurs here. There is no reason why the concomitant evaporation and liquefaction, of which we have spoken, should take place if the gaseous air in *r* and the liquid air in *v* are one and the other at atmospheric pressure; moreover, so that the liquid should bring about the liquefaction of the gas, it is necessary that it shall take heat from it: it is necessary, therefore, that its boiling temperature should be lower than the temperature of liquefaction. But we know that under the same pressure the boiling temperature of the same fluid is equal—and not inferior—to that of liquefaction. For example, water boils at  $100^{\circ}\text{C}$ . under atmospheric pressure and its vapour also liquefies under this same pressure precisely at  $100^{\circ}\text{C}$ .

To accomplish this transference of heat from the gas to be liquefied to the liquid to be evaporated, it is requisite to *lower* the temperature of ebullition of the liquid,\* or, what is the same thing, *raise* the temperature of liquefaction of the gas, which can be attained by *compressing* it. But, as Parkinson perfectly understood, and as we have shown in our experiment just above, it is not a question now of high pressures such as we found necessary to liquefy air by expansion. A simple compression of one effective atmosphere raises the temperature of liquefaction of the air

\* Which can be attained by making a partial vacuum over the liquid, the cause of a lowering of temperature whose intensity may be appreciated by referring to the curves (Fig. 70).

#### 4 SEPARATION OF THE AIR INTO ITS ELEMENTS

about  $8^{\circ}$  C., and therefore produces a sufficient difference of temperature between the gas and the liquid to abundantly provoke evaporation and liquefaction concomitantly.

In practice, however, 1 atmosphere would prove insufficient: seeing that air is a heterogeneous fluid, neither its temperature of liquefaction nor its temperature of vaporation are invariable.

The result is, that though air testing 21 per cent. can commence to liquefy *without* pressure in liquid air testing 1 per cent.—since, as we shall see, it commences to condense when still 47 per cent. less volatile than the external air, 1 per cent.—the necessity for evaporating these progressively richer liquids, and finally pure oxygen, involves a progressive increase of pressure, so that this progressive elevation of the temperature of the liquid, which is, we know, the reason itself of the separation, is at the same time the *measure of the expenditure of energy* foreseen by theory (p. 279).

In practice it is, therefore, necessary to impart to the air to be liquefied a sufficiently high pressure to raise its temperature of liquefaction, not only above  $-193.5^{\circ}$  C., the normal temperature of ebullition of liquid air, but above  $-182.5^{\circ}$  C., extreme limit attained when the liquid which is evaporated is pure oxygen. To this end some 3 to 5 atmospheres more or less, according to the desired rapidity, are required, and it is effectively this pressure which is in general use.

We can see, from now onward, that the separation of the elements of the air can in no case cost nothing, since it necessitates a slight compression of the air to be treated.

**Necessity for the addition of cold.**—But a further circumstance still intervenes, acting identically in the same direction.

As is the case with all industrial operations, and with all human undertakings, we might say, the recuperation of

imperfection itself of the exchangers of temperature and the inevitable penetration of the heat of the environment.

Consequently, the quantity of liquid air which is reconstituted at each instant *is not altogether equal* to that which is evaporated. There is a constant loss in the quantity of liquid air, and it is indispensable to make good this loss by means of *added* liquid air furnished from some external source.\* It is naturally a liquid air machine identical with those we have described which is used for the purpose, and we thus see the double part that the liquid air machine plays in the manufacture of oxygen: manufacture of the initial liquid air required for filling the apparatus and then manufacture of the liquid air to make good the losses.

But, if the loss of liquid air is inevitable, it is notably slight—much less than many readers might certainly imagine. The temperature exchangers, moreover, are such remarkable appliances, that while receiving the evaporated gases about  $-180^{\circ}\text{C.}$ , they deliver them at a temperature hardly less than  $5^{\circ}$  to  $10^{\circ}\text{C.}$  below the temperature of the environment. Let us say  $10^{\circ}\text{C.}$  This corresponds to a loss of cold of hardly 2.5 therms per kilogramme of air treated.

Now a single kilogramme of liquid air added (p. 308) implies 100 available frigoria, and admits, therefore, of the treatment of 30 to 40 kgrm. of atmospheric air.

In other words, and to express matters in a more catching form, if the recuperation is not perfect, it falls so little short that thirty litres of liquid air, by evaporating, will reconstitute *twenty-nine* in a well-constructed apparatus. This marvellous result gives a high idea of the efficiency of those admirable instruments which constitute exchangers of temperature, and it is this which is the whole secret of the enormous economical range of the industry with which we are dealing.

\* We shall see (Chap. XVIII) that it may be convenient to replace this source of added liquid air by doing away with the air to be treated, combined with

Let us return to the diagrammatic apparatus we described just now. We now find that to place it in normal working order, the vaporiser *v* being full of liquid air produced by an expansion machine, it is sufficient to pass into the tubular system some air compressed to the slight extent, the necessity for which we pointed out above, and cooled initially down to the temperature of liquefaction by its passage through the exchanger *E*. This air is liquefied while bringing about the progressive evaporation of the external liquid air. The evaporated gases, whose cold is retained in the exchanger by the compressed air which enters, are therefore enriched progressively in oxygen. As soon as their test attains the value considered sufficient they are collected. The evaporation ended, the collector *c* is full of recuperated liquid air. It is then, by means of the pressure which exists in the tubular system *F*, passed to the evaporator *v*; the quantity of additional liquid air, furnished by the expansion machine, is added which is sufficient to reconstitute the amount of initial liquid and we commence again.

Under this form the apparatus is perfectly rational. It only requires to become wholly industrial to exchange the latent discontinuity of the above working for the continuity of manufacture which is required in practice. It is easy to arrive at this result, for example, by means of the following device (Fig. 113).

Here the liquefying tubular system is of an elongated form and disposed horizontally in the vaporiser *v*; the compressed cold air reaches the tubular system at *A*. The liquid air produced is collected at *B* and delivered through *C* in a continuous way, by reason of its pressure, concurrently with the additive liquid air which arrives through *D*. The liquid in *v* is progressively evaporated in contact with the tubes of the system, and, as it is evaporated, advances towards *D*. The evaporated gases



are therefore the richer in oxygen the further they are produced towards D.

These only will be collected for use which are evolved from the point E where the test is considered sufficient. We require here two exchangers, the one M to maintain the cold of the poor gases, the other N to recuperate that of the superoxygenated air. When the apparatus is in work-

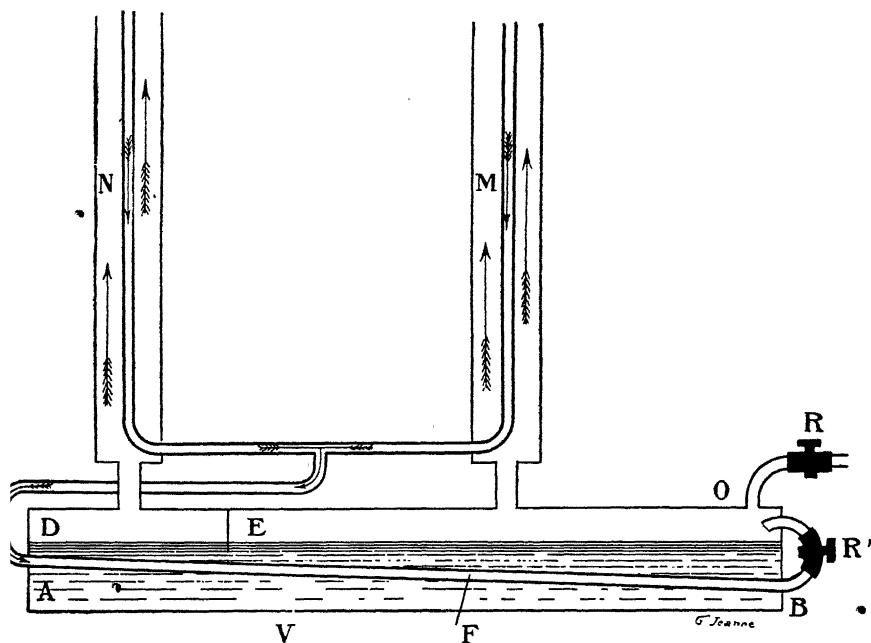


FIG. 113.—Continuous apparatus for fractional evaporation.

ing order, each of these two exchangers is adjusted in such a way that it transmits automatically a portion of the total compressed air equal to the portion of the evaporated gases which it has to heat.

Such is, in general terms, the idea which we are able to form of a rational apparatus for the manufacture of superoxygenated air. Doubtless progressive evaporation continues still, with its gross defects, and with the deplorable yield which it implies when it is applied to the production of

## 8 SEPARATION OF THE AIR INTO ITS ELEMENTS

very rich oxygen; but, we know to what an enormous extent the addition of recuperation diminishes the cost of the operation, the air of the separation circuit being entirely liquefied, through compression to 3 or 4 atmospheres, we finally arrive at something which is wholly acceptable and wholly industrial.

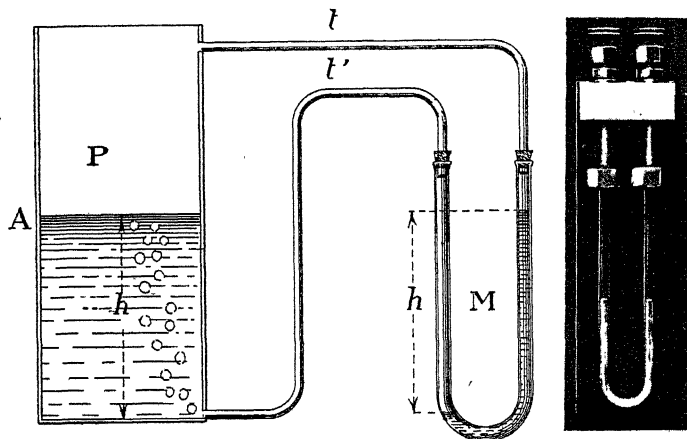
**Gauges for liquid air.**—We must not terminate this description without saying a few words about instruments which render the most essential service in connection with all the apparatus above described, and without which it would be nearly impossible to understand what takes place in them and to be sure of their working. We speak of the special gauges to indicate the liquid level, the first idea of which is due to Hampson, and the absence of which on Claude's first apparatus was not one of the least causes of inconvenience and lack of success in his first attempts. Among the many problems which required solution to put these appliances in working order, this was doubtless one of the most important.

It can be easily understood how useful it may be to know exactly at each instant the quantity of liquid air available in, for example, an oxygen apparatus, so as to know whether this quantity is increasing or diminishing, and to regulate the addition of cold accordingly. We can understand to what extent it is likewise necessary to know the level of the liquid air in the collectors of the recuperated liquid, to secure a proper opening of the ascending valves, and to arrange so that the reconstituted liquid air shall be evacuated as exactly as possible as and when it is produced. Now the problem of externally indicating the height of the liquid air in a recipient which is completely closed, and which is generally surrounded by a thick layer of insulating material, is manifestly very different from what it

steam boilers and based upon the principle of communicating recipients, besides being probably condemned to breaking when put in use, would be constantly covered by a thick coat of rime, unless protected by double or triple vacuum walls.

The following is the much more elegant solution which is in use. The problem is to know the liquid air level in the recipient *A*, which is closed on all sides (Fig. 114), and in which may obtain, on the other hand, a certain pressure *P*.

Through a metal tube *t* the upper part of *A* is placed



FIGS. 114 and 115.—Level indicator for liquid air. Model used by the "Liquid Air Company."

in communication with one branch of a differential water gauge *M*. By another tube *t'* the lower part of *A* is similarly in communication with the other branch. The liquid in *A* tends to drain into the tube *t'*; but, as it comes into contact with warmer parts, it evaporates therein. Now the evaporated gas can only escape in two directions: towards *M*, but this road is barred by the liquid in *M*; or towards *A*, and on this side the evaporated gas can effectually escape in bubbles through the liquid, but it is indispensable to effect this, that the pressure of this gas should equal the pressure  $P + h$  of the liquid it displaces. The pressure of

the gas in  $t'$  is therefore  $p + h$ ; the pressure in  $t$  on its side is equal to  $p$ : it results therefrom that the liquid in  $m$  is driven into the right-hand branch to an amount exactly equal to  $h$  if the density of the liquid exactly equals that of liquid air, which is very closely the case with water.

When the height  $h$  is too great the water is replaced by mercury, and we then obtain the height of the liquid by multiplying by 13 the difference in level of the mercury.

## CHAPTER XIV

### VARIOUS PROCESSES FOR PROGRESSIVE EVAPORATION

**Linde's first process (1895).**—The honour of having first succeeded in the practical manufacture of oxygen with the aid of liquid air belongs to Professor Linde, whose process for the liquefaction of air, which we have described long since, was in fact completed by an arrangement for the manufacture of oxygen.

Here is, in accordance with the description itself in the French patent,\* the working of this apparatus (Fig. 116):

“ $C$  is a compressor, by means of which the air pressure is increased from  $p^1$  to  $p^2$ , the temperature rising at the same time from  $t^1$  to  $t^2$ .

“The air then passes through the cooler  $K$ , in which a certain quantity of heat is removed therefrom by cooling water or by any other suitable source of cold, so that the temperature of the air is reduced from  $t^2$  to  $t^3$ , the pressure remaining constant at  $p^2$ .

“In this condition the air is passed into a reverse current  $G^1$  working as perfectly as possible and protected as efficiently as possible from all absorption of heat from the exterior. By means of the passage of the air through the apparatus  $G^1$ , the temperature of the air is lowered still further to  $t^4$  for reasons explained below. At the lower extremity of the reverse-current apparatus  $G^1$  is placed a regulating valve  $R^1$  through which the air passes into the recipient  $V^1$ , which is also carefully protected against all absorption of external heat, and in which the pressure

\* Corresponding with German patent 88824 of June 5th, 1895.

equals  $p^1$ . After escaping therefrom the temperature of the air will be  $t^5$ , which will be so much lower than  $t^4$  the greater the difference  $p^1 - p^2$  and the lower the temperature  $t^4$ . The air with the actual temperature  $t^5$  is passed into the reverse-current apparatus  $G^1$  in the contrary direction to the arriving air, whose temperature is consequently reduced before it passes out, so that these two temperatures  $t^4$  and  $t^5$  mutually lower each other until through the introduction of heat from the exterior or through the liberation of heat in the interior, equilibrium is established. This last condition is produced as soon as the cooling is advanced to the point of condensation of the atmospheric air, where liquefaction commences and at which some latent heat is given off. When equilibrium is established a perfectly definite portion of the escaping air, which is regulated automatically, is collected in the liquid state in the recipient  $V^1$ , while the remaining portion which is in the gaseous state returns through the reverse-current apparatus to the compressor  $C$ . The liquid collected in the recipient  $V^1$  passes through a second regulating valve  $R^2$  to the recipient  $V^2$ , in which the pressure is that of the ordinary atmospheric air  $p^0$ .

"Following upon the reduction of the pressure  $p^1$  to  $p^0$ , a portion of the liquid, to wit a portion of the nitrogen, is evaporated. When heat is introduced subsequently in the liquid contained in the recipient  $V^2$  by causing more or less air to pass through the worm  $S$ , whose pressure has been brought by the compressor  $C$  to  $p^2$ , the evaporation of the nitrogen may be continued at will, and thereupon the remaining mixture of oxygen (or pure oxygen as the case may be) can be withdrawn through the valve  $h$ .

"The nitrogen escaping at  $A$  exchanges in a reverse-current apparatus  $G^2$  some of its heat with the arriving liquid air.

"When we want to obtain oxygen not in the liquid but

in the gaseous form, the liquid is passed through a reverse-current apparatus  $G^3$  in a contrary direction to a third portion of compressed air, the heat required to evaporate and warm the oxygen being taken from the compressed air. In this way we are enabled to effect a complete recuperation of the cold expended in cooling and liquefying the air, and the machine has only to produce the cold necessary to make good the losses.

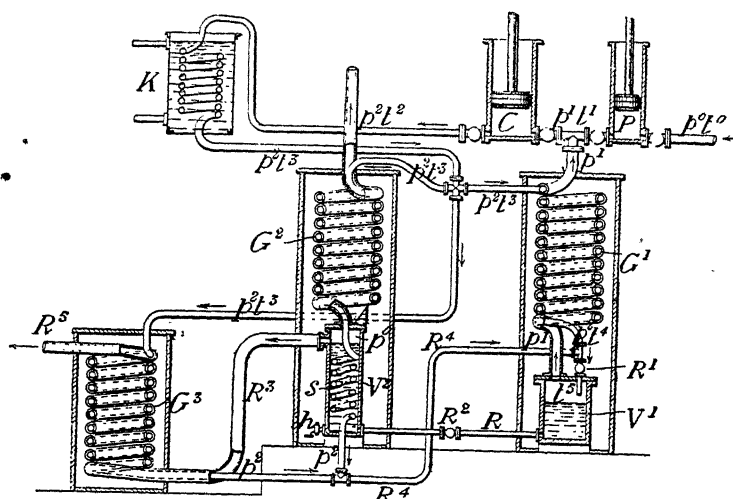


FIG. 116.—Linde's oxygen apparatus (1895).

“The feed pump  $P$  serves to charge the machine with air and to replace the liquid air.

“The yield of the present machine depends essentially upon the perfect action of the reverse currents in the three apparatus  $G^1$ ,  $G^2$ ,  $G^3$  and upon the insulation of the apparatus as well as of the recipients  $V^1$  and  $V^2$  against all absorption of heat from the outside.

“As is shown in the figure, each of these apparatus is formed of two pipes of considerable length (for example some 100 metres) placed one in the other, and twisted together into a spiral, and mounted on wooden supports; the different pieces being insulated one from another and

from the outside by a good insulating material (for example raw sheep's wool)."

We see that we have here, realised practically for the first time, the essential elements of our combination type :

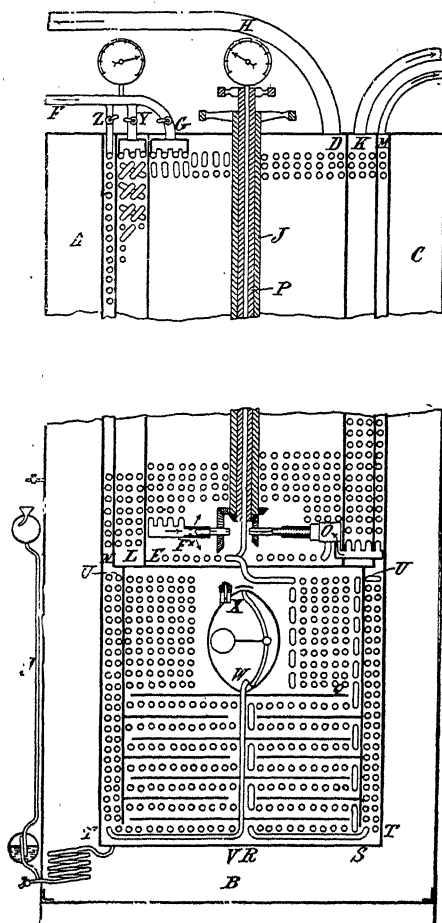


Fig. 117.-- Hampson's oxygen apparatus (1896).

the source of evaporating heat being furnished, by the atmospheric air itself, to be treated, with efficient recuperation of cold, the cold of the gases being retained in the exchangers by the entering compressed air, and the cold of evaporation being equally retained; finally an expansion circuit



designed for the manufacture of the liquid air for filling up and replenishing.

We have to salute in this apparatus the archetype of all the present machines, which was the first to work *effectively* in many installations, and which was the first to prove that the commercial obtaining of oxygen through liquid air was possible.

**Hampson's process (1896).**\*—The compressed air to be treated, initially cooled in exchangers of temperature  $G, D$  is delivered to two expansion valves. One  $F$ , permits of wholly expanding a portion of the air down to atmospheric pressure and of furnishing the additional cold necessary to cover the losses.

The second valve  $O$  simply causes the remainder of the air to suffer a fall of pressure, which brings it to the pressure of liquefaction in the spiral pipes submerged in the liquid of the successive superposed trays  $Q, V, R$ . The liquid formed in the tubes is emptied by a system of floats  $XW$  on to the trays, and is enriched more and more with oxygen through its evaporation (and also through rectification) in its descent to the successive trays. It arrives at the condition of sensibly pure liquid oxygen and is evaporated as such in the peripheral compartment  $UT$ .

We see that the addition of cold, which in Parkinson's process was furnished by auxiliary liquid air, is realised here partly through the complete expansion of a fraction of the air employed, partly by means of an expansion of the air treated between the initial pressure and that of liquefaction.

**Thrupp's process.**—We have already said a few words (p. 159) about the expansion device with external work invented by this engineer. His patent relating to the manufacture of oxygen† is also distinguished by original peculiarities.

\* English patent No. 7559 of 1896.

† French patent 307841 of 1901.

Through the liquid which it is intended to evaporate to extract its oxygen, atmospheric air is first made to bubble without pressure, this being already cooled down to the temperature of liquefaction by its passage through an exchanger of temperature. Through this bubbling, a phenomenon of *rectification* is produced, which we will utilise further in a continuous way. The more volatile nitrogen in the liquid evaporates and *condenses* an exactly

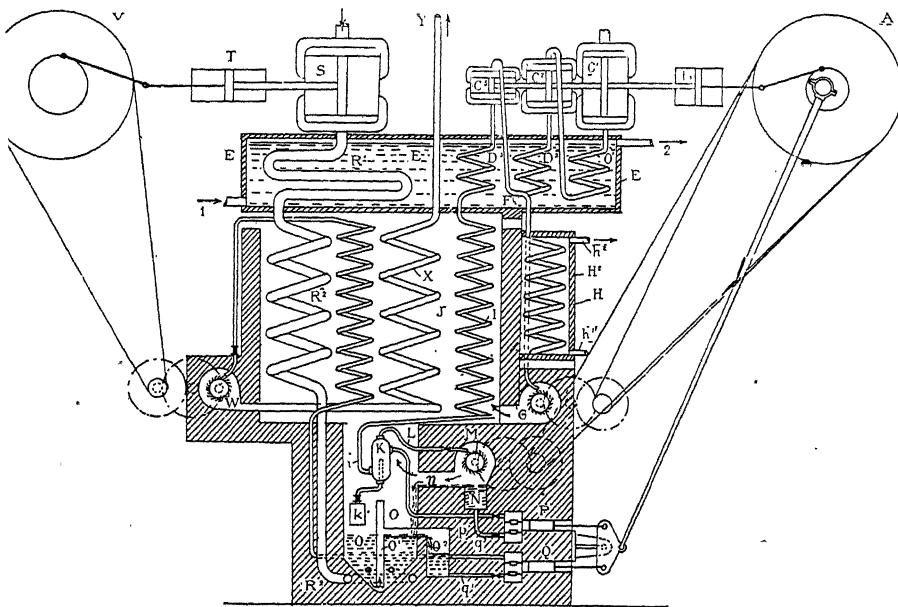


FIG. 118.—Thrupp's apparatus (1901).

equivalent quantity of oxygen from the bubbling air. It is premised that it is the exhausted air and the evaporated nitrogen whose function it is to cool the air used for bubbling in the above exchanger. The test of the liquid in oxygen increases in this way without its *quantity* diminishing as in the ordinary progressive evaporation. We gain, therefore, some additional oxygen which we can in certain respects consider as gratuitous, since it is furnished by the air without pressure, used for bubbling.

Unfortunately it is wholly impossible to arrive at pure oxygen by this process. We shall see, moreover, that the 21 per cent. air which we employ cannot enrich liquid air through which it bubbles, save up to the limit of 47 per cent. From 47 per cent. to 100 per cent. the evaporation with the accompanying liquefaction has to be completed by the habitual barbarous methods, decorated in this case with a wealth of expansion turbines, *M*, *G*, *W*.

**Pictet's process (1899).**—The air to be separated, compressed to a slight pressure, is cooled down to its temperature of liquefaction by circulating through exchangers in a contrary direction to the products separated (Fig. 119).

It passes then to be liquefied into a long tubular system *JK* submerged in successive compartments  $I_1I'$ ,  $I_1I'_1$ , full of liquid air and placed one over the other. The liquid which is formed, collected at the lower end, and freed in the filters  $L L_1$ , from the solid carbonic acid which it contains, is continually emptied, thanks to its pressure, into the upper compartment, whence the non-evaporated excess falls into the compartment below it and so on, arriving in the lowest compartment in the condition of pure oxygen as in Hampson's machine.

The evaporated gases are thus the richer the lower the compartment in which they are produced. They are collected through a first exchanger *S* as super-oxygenated air—which the author calls *industrial oxygen*—at the level of the compartment selected as suitable; through a second exchanger  $P_1$  as ordinary non-usable air; finally through a third *O* as air rich in nitrogen.\*

The patent, according to Pictet, covers in a general fashion concomitant evaporation and liquefaction at *low pressures*. It would be neither more nor less than a patent of monopoly placing the atmosphere at the exclusive service

\* French patent 295002, December 6th, 1899. This process was described by Pictet to the Society of Civil Engineers in June, 1901.

## SEPARATION OF THE AIR INTO ITS ELEMENTS

Pictet. In the patent dated from the first and clamorous  
cess of its author (p. 62) such a claim might be com-  
prehensible.

But it only dates back to 1899, and is posterior to the

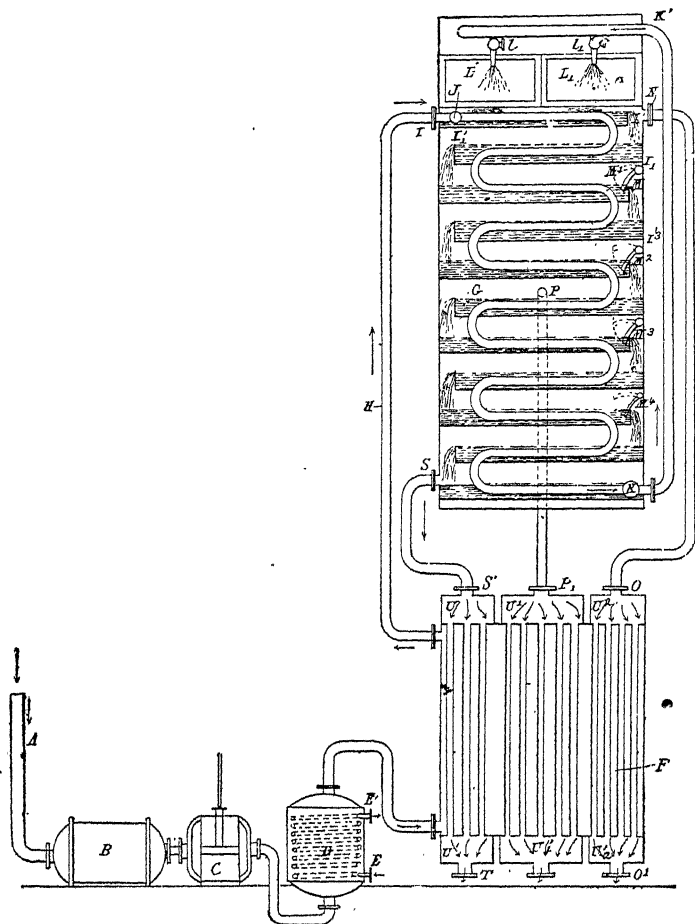


FIG. 119.—Pictet's apparatus (1899).

efforts of numerous inventors; it leaves out of considera-  
tion, among others, Parkinson and Hampson, and forgets  
the fact, otherwise manifest to every physicist, that the  
liquefaction of atmospheric air under slight pressure in  
liquid air which is evaporating was already known, described

and industrially applied—witness Parkinson's *ventilator* (p. 309).

But no matter!

Because at the risk of astonishing physicists, here is what Pictet—after having, by the way, shown that when air is liquefied progressively, it is the *nitrogen* which liquefies first—here is what he asserts is the fundamental point of his invention.

All those who have been, or are, preoccupied with the problem of the extraction of oxygen through liquid air know that one of the greatest difficulties of the problem is to replace the liquid air as and when lost, the essential and subtle raw material for the operation. As Claude, moreover, called attention thereto (p. 315), there is always a certain loss due to the unavoidable imperfection of the apparatus, so that, however remarkable the efficiency of the processes for the recuperation of cold may be, there is always *more* liquid air expended than that reconstituted. We must obtain the difference, either from an auxiliary source of liquid air, or from an excess pressure in the air to be treated, the expansion permitted by this excess pressure being the compensating source of cold, and it is the totality of these two means which Hampson and Linde employ.

Now, while all his competitors found the greatest difficulty in avoiding a very troublesome drought, Pictet was inundated with liquid air, so flooded as not to know what to do with it.

And how is it that he was so privileged?

In this wise: his competitors, the slaves of the imperfections of all human processes, reconstitute at each instant *a little less* liquid air than they evaporate. Pictet, on the contrary, insists throughout the whole course of his patent on the fact that he recuperates *a little more*.

“This is the capital fact in the new method we are dealing with, and which has not yet been utilised in manufactures.”

It should be noted that Pictet founds his marvellous system upon a well-known physical law. This law is that the heat of liquefaction or of evaporation of a fluid *diminishes* with the pressure, to become *nil* at the critical point, where we, moreover, know the passage from the liquid to the gaseous state is effected indifferently, without variation of volume or absorption of heat.

Therefore the heat of liquefaction of air under pressure being less than the heat of evaporation of the external liquid, *more* will be liquefied than evaporated, supposing that the gas to be liquefied is really at its temperature of liquefaction. This is perfectly correct.

Only this is not all. The cold-producing value of liquid air, in virtue of which it is able to liquefy gaseous air, is measured by its heat of evaporation, but as this under the same pressure, is equal to the heat of liquefaction, to say that the latter is less in the air which is condensing is to say that the cold-producing value of liquid formed under pressure is also less. It is for this reason, and it can only be for this reason, that more is produced.

But when the liquid, according to the usual process, is delivered in the vaporiser to produce in its turn the condensation of the air to be treated, its heat of evaporation increases since it falls to atmospheric pressure. Improved in *quality*, is it going to preserve its *quantity*?

Not at all; it partially evaporates, at the moment when it passes to atmospheric pressure, this evaporation furnishing the cold corresponding to the lowering of the boiling-point and paying the cost of the improved quality; the quantity thus evaporated exactly absorbs all the excess liquid which Pictet put down to gain.

As to the internal work of expansion corresponding to the slight pressures patronised by Pictet, it is undoubtedly best not to take it into account, since, as always, its real effect must be determined only by the slight imper-

fection of the air at the *entering* temperature in the exchangers—which no pains are taken in this case even to lower.

Thus, the definite quantity of liquid air produced will be barely equal theoretically to that of the liquid evaporated. And as, furthermore, Pictet has to fight in practice against the imperfections of his apparatus, it follows that, like the rest of the world, he reconstitutes notably less liquid air than he evaporates, and that, like the rest of the world, he has to have recourse to a source of cold. It is absolutely impossible that his apparatus should run itself, as he never ceases to assert throughout his patent, so that the point considered as vital, the only one which effectively distinguishes the process from its predecessors, that which would permit of concomitant evaporation and liquefaction to be sufficient unto themselves, notwithstanding the low pressure, implies the complete impossibility of working.

## CHAPTER XV

### ACCELERATED LIQUEFACTION OF THE OXYGEN OF THE AIR

WE have now arrived at the personal work of Claude in the problem of the separation of the elements of the air.

In all the above processes, the air to be treated is completely liquefied as a preliminary in a single mass; no separating action on the elements is therefore brought about during the first phase, and it is entirely through the eventual evaporation of the 21 per cent. liquid thus obtained that the separation is effected.

An inexact generalisation deduced by Sir J. Dewar from one of his experiments has been the origin of this manner of treatment, whose faults we will demonstrate below. This was the experiment in question\*:

Some gaseous air contained in glass flask B fitted with a bent tube is plunged in liquid air R (Fig. 120) which which boils in a vacuum.

A portion of the air in the flask is condensed in the bent tube by reason of the very low temperature which prevails there. Now we observe that the liquefied portion has the *same composition* as normal gaseous air, that is, 21 per cent. oxygen and 79 per cent. nitrogen.

Professor Dewar concluded from this experiment, contrary to the opinion expressed by Professor Ramsay, and already contested by him, that when air is called upon to pro-

\* 'Proc. Roy. Inst.,' February, 1897.

† 'Proc. Chem. Soc.,' December, 1894.



gressively liquefy, its two elements, in contrast to what takes place in evaporation, are *simultaneously* liquefied in the invariable proportions constituting atmospheric air.

The consequence of this theory from the point of view of the processes which we are studying is evident in the absence of all selective effect when liquefaction takes place; the necessity to push this to an end is imperative to *totally* liquefy the air treated, and to expend all efforts for separation on the ulterior evaporation of the 21 per cent. liquid

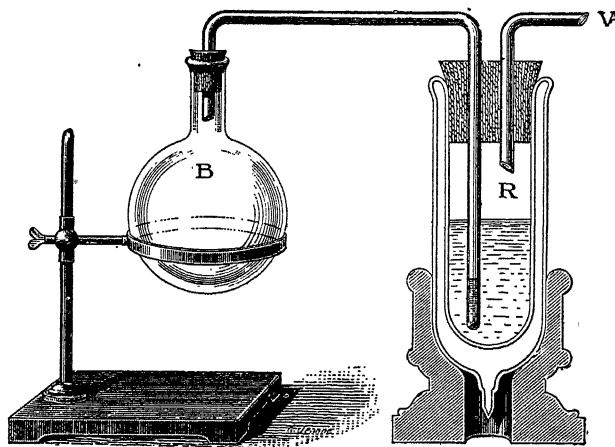


FIG. 120.

thus obtained; this is, in effect, as we have seen, the formula of all the systems previously described.

Pictet himself had no chance of escaping therefrom, notwithstanding his audacious theory of the accelerated liquefaction of the nitrogen, which certainly presupposed partial selective effect, but which also obliged him to entirely liquefy his air to make him master of the whole of the oxygen.

This state of things became one of Claude's preoccupations from the beginning of his investigations. The air experiencing in the course of treatment two inverse operations—one of liquefaction, then one of evaporation—it appeared

to Claude to be a matter of great regret that the liquefaction could not be turned to account for separation on the same footing as evaporation, which would have been *à priori* the source of very important advantages, which we will define further on.

Certainly Claude was surprised at the ante-physical presentment of Dewar's theory. As a general thesis the phenomenon of liquefaction is always the inverse of that of evaporation, and for the air to behave otherwise it would have been necessary that in this case there should have occurred a very curious anomaly indeed.

However, he was unable at starting to rebel against such a well-authorised opinion, so generally expressed and received by competent authorities in the matter. All his previous efforts had tended to relieve him from conditions where this was applicable, by carrying out condensation at pressures permitting of a temperature of liquefaction superior to the critical temperature of nitrogen, and where he considered that it was inevitable that the oxygen would be liquefied preferentially during the early stages.

He observed in passing—with some satisfaction—that it was in this patent, taken out in France on April 9th, 1900,\* that the first idea is found of the mechanism of *rectification*, whose application to liquid air was to bring about later such excellent results (Chap. XVIII). But this patent presupposed the solution of the problem of the liquefaction of air, and it has been explained at some length in the preceding pages with what difficulties Claude was beset to solve this question. More and more preoccupied by his successive failures, he arrived at the point of putting on one side all that was not directly related to the solution of the problem sought for; it was only subsequent to the success of his efforts in May, 1902 (p. 164), that he was able anew to occupy himself with oxygen.

\* French patent 299051.

With some reflective help he was not long in becoming definitely convinced that the theory of the simultaneous liquefaction of the two elements of the air was too illogical to be true. His reasoning, moreover, drew the most essential part of its conviction from simple common-sense. If, when liquid air is evaporated, nitrogen is given off preferentially the first, it is because it is the more volatile, therefore, apparently, the more difficult to condense; if the oxygen remains the last in the liquid state, it is because it is less volatile, therefore probably the easier to condense. If, therefore, we constrain some air to progressively liquefy, it is impossible to see how oxygen could help liquefying preferentially in the first stages, and how nitrogen should not preferentially remain in the gaseous residue. And if it appears to act otherwise in Dewar's experiment, it is simply because the air is obviously not in the condition of *partial* liquefaction in the proper signification of the term, which requires that all the molecules of the gaseous mass shall be simultaneously submitted to the temperature which has to produce the selection, but in the case of a *total* liquefaction, of the portion which penetrates to the appendix.

Such is the theory—if the word be not too ambitious—that simple common-sense suggested to Claude; and if he is obliged to recognise that as far back as 1900 he was anticipated in this way of looking at the matter without knowing it by the erudite Canadian, Le Sueur, in an interesting patent to which we shall have to refer further,\* at least Claude had the great satisfaction to be the first to furnish a clear experimental proof thereof in an experiment carried out in 1903, the results of which he communicated in 1903 to the Academy of Sciences.†

“The experiments were carried out with the help of a liquefying apparatus composed of a bundle of tubes im-

\* Canadian patent No. 74430 of May 21st, 1900.

† ‘Proceedings,’ June 29th, 1903.

mersed vertically in the liquid air of a recipient holding from 7 to 8 litres. The bundle was attached at its upper end to a source of low-pressure compressed air across a temperature exchanger cooled preliminarily through the manufacture of a certain quantity of liquid air to  $-160^{\circ}\text{C}$ . The lower end of the bundle was finished off by a collector furnished with a draw-off cock.

"A first experiment consisted in allowing the cold compressed air, reaching the bundle of tubes with the effective pressure of 2.5 to 3 atmospheres, to be *entirely* liquefied in the apparatus, and to draw it off when the bundle was full of liquid. This experiment naturally furnished a liquid of composition sensibly identical with that of the atmosphere, or 23.8 per cent. owing to a slight evaporation occurring at the drawing off.

"A second experiment was carried out by withdrawing the liquid air as it was produced and by opening the draw-off cock sufficiently to at the same time get rid of a portion of the non-liquefied gas and thus avoid the accumulation of the more refractory product. This trial, repeated three times, furnished liquids which were highly oxygenated, testing respectively 36, 42 and 48 per cent. of oxygen, according to the quantity of gaseous air removed simultaneously, this quantity being very large in the third trial.

"The difference is so large that it cannot be attributed to evaporation at the time of withdrawal, and the higher limit of 47 per cent. is exactly that which we might have anticipated from an examination of Baly's curves (Fig. 110), supposedly applicable to the phenomenon of condensation, since according to these curves, to a gas testing 21 per cent. there corresponds a liquid testing 47 per cent."

Thus Claude's tests confirmed him in his idea. As in all known cases the phenomenon of the condensation of the gaseous mixture which constitutes the air is the inverse of that of evaporation, if air is called upon to liquefy progres-

sively, the first portions which are liquefied are the richest in oxygen, and, in point of fact, Baly's curves appear to be applicable for the prediction not only of the peculiarities of evaporation, but also of those of liquefaction.

Truly, the theory which was at that time the object of Claude's criticism would not have even been propounded without the authority which it claimed, and the very simple and very correct conception of Sir W. Ramsay would have imposed itself quite naturally, for, as we shall see, the liquefaction of gaseous mixtures has been the occasion of important work and of conclusions of accurate precision. But we know what a tendency there has been to suppose that liquid air, because of the extremely low temperatures which it brings into play, enables us to penetrate into a new world where the ordinary laws of physics no longer retain even rights of asylum; we know also, on the other hand, how much more difficult it is to extirpate an error which has acquired the rank of admitted truths than to impose a new truth. This was the case to such an extent that the theory of simultaneous liquefaction still numbers its adherents,\* and still serves as the basis—excepting Claude's—of all the present oxygen apparatus. This is what gives some value to the ideas which he has put forward and some excuse for these lengthy explanations.

\* It was not without some surprise that Claude noticed that Sir J. Dewar on a recent occasion persisted in his original opinion, alleging that no proof had yet been advanced of its inexactitude.

## CHAPTER XVI

### SOME CONSIDERATIONS ON THE LIQUEFACTION OF GASEOUS MIXTURES

BEFORE going further, it will be useful to place matters on a precise footing. We have seen in the first part of this work how simple gases behave from the point of view of their liquefaction. Gaseous mixtures follow entirely different laws, which it is necessary for us to know.

This question has been the object of numerous works, to which are more specially attached the names of Cailletet, Van der Waals, Gibbs, Kuenen, Mathias, Duhem, Caubet, etc. Nevertheless, in spite of the very exact and very important results obtained by these experimenters, it does not appear, after what has preceded, that their somewhat complex theories have not only not taken their place in classical courses, but have not even reached the knowledge of a number of eminent physicists.

We can hardly, on any other ground, explain the extraordinary assertions which have been made concerning the liquefaction of air.

We propose, therefore, to gather the essential facts as briefly as possible from these works, or at least those among them, the knowledge of which will be the most useful to us in the sequel of this work.

And, more especially, since the well-defined objective towards which we are working admits of our making without more ado some restrictions calculated to considerably facilitate our undertaking.

(1) We are only considering mixtures formed by gases which in the liquid state are mixable one with the other in

all proportions; this is the most general and important case, and is particularly the case with the elements of the air.

(2) We are only considering furthermore, in the formation of these mixtures those gases whose aptitude for liquefaction differs notably, that is, whose curves of vapour tension are very far removed from each other (Fig. 121). This presupposes that the critical temperatures  $Om$  and  $On$  are sufficiently different, and that at the same temperature lower than the lowest critical temperature, the two gases considered isolatedly, liquefy under very unequal pressures.

In the case of mixtures of gases possessing curves of

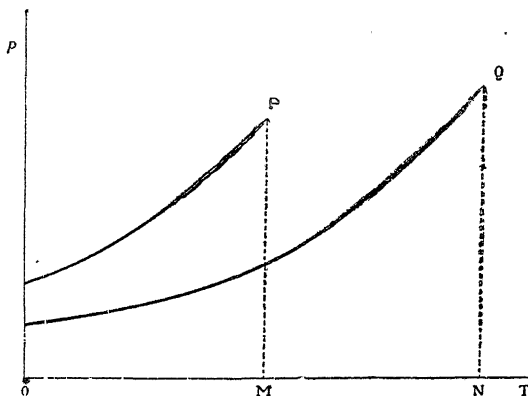


FIG. 121.—Gases with very different aptitudes for liquefaction.

vapour tension very close together, the notion of greater or less aptitude for liquefaction becomes very ambiguous. As for example, Curves I and II (Fig. 122), corresponding to two gases whose respective critical points are at  $m$  and  $n$ , and whose vapour tension curves, otherwise very close together, intersect at  $a$  at a very acute angle: the fluid II is more volatile than I, for all temperatures comprised between  $Om$  and  $On$ , since for all these temperatures it is below its critical point. It is less volatile, on the contrary, for all temperatures comprised between  $On$  and  $Oa$ , and becomes again more volatile at temperatures below  $Op$ .

We ought to add to this, in the case of the mixture of

these gases, the influence of the possible reciprocal affinity of their liquids, and we can easily understand that the results relating to these gases may be very complicated.

These two conditions, to which Fig. 77 also bears witness, are very sufficiently complied with by the constituents of the air, their respective critical points being  $-118^{\circ}\text{C.}$  and  $-146^{\circ}\text{C.}$ , and their respective liquefaction pressures at  $-146^{\circ}\text{C.}$ , being 13½ atmospheres for oxygen and 34 for nitrogen (33 according to Travers). The restriction is therefore legitimate.

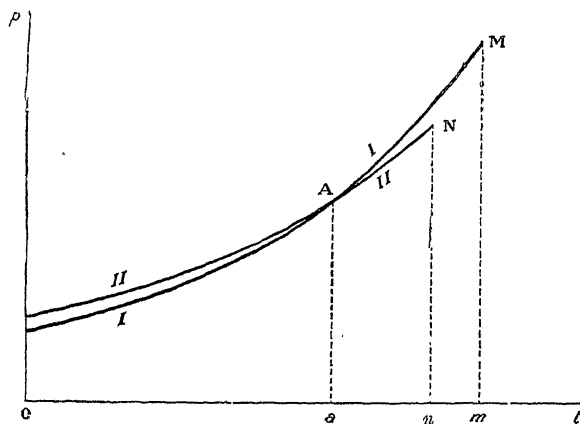


FIG. 122.—Gases with aptitudes for liquefaction lying very close together.

**Liquefaction of gaseous mixtures at constant temperatures.**—Let us consider a mixture of two gases which satisfies the conditions we have just laid down; we shall designate by  $L$  the more liquefiable element (oxygen in the case of air); and by  $V$  the less liquefiable element (nitrogen in the case of air); we shall call the *test* of the liquid or gaseous portions the percentage of  $L$  in these liquids or gases.

This premised, there exists a certain temperature—or, rather, a certain zone of temperature (a remarkable region which has been designated the *critical zone*)—above which all complete or partial liquefaction of the mixture is impossible within the temperatures of the critical zone itself;



and a part, but only a part of the mixture, can be brought by pressure to the liquid state. This is the singular region of *retrograde condensations*, an upside-down world where condensation is produced by diminution of pressure, and evaporation by increase of pressure!

Finally, for temperatures inferior to those of the critical zone, and in this far simpler case, which is the only one with which we shall occupy ourselves here, it is always possible to bring *the whole* of the mixture to the liquid state by the effect of sufficient pressure.

But, a capital fact, the knowledge of which will itself alone enable us to foretell the majority of the peculiarities of the liquefaction of these mixtures: experience shows that the liquefying temperature at constant temperature, differing in this respect from that of simple gases, is not itself *constant* from one end to the other of liquefaction.

Far from it.

Without doubt, as with simple gases, we have to reach a certain pressure to obtain the temperature of the experiment, inferior to the temperatures of the critical zone, the first drop of liquid (the *dew-point* of Duhem); but if we limit ourselves to this pressure, we shall only obtain this single drop of liquid; to obtain more, it will be necessary to *augment* the pressure a little, and raise it still further to finally liquefy the last gaseous bubble (*boiling-point* of Duhem). Some examples will suffice to show the importance of this phenomenon.

The mixture of 38 per cent. in volume of  $\text{SO}_2$  with 62 per cent.  $\text{CO}_2$ , studied at the temperature of  $46.2^\circ \text{C}$ . by Caubet,\* yielded a first drop of liquid (dew-point) under a pressure of 21.8 atmospheres; but liquefaction was only completed (boiling-point) at 59.6 atmospheres.

According to the same investigator, the mixture of 32 per cent. chloride of methyl with 68 per cent.  $\text{CO}_2$ , studied

\* 'The Liquefaction of Gaseous Mixtures,' by F. Caubet. Publisher: Hermann, Paris, 1901.

at 60°, attained its dew-point at 47 atmospheres and its boiling-point at 80 atmospheres.

This increase of pressure during liquefaction is a general fact. It is, on the other hand, *continuous*, and does not import sudden inflections, whether the liquid progressively formed be withdrawn as formed, or whether, on the other hand, the *liquid phase* (as it is styled) be left to accumulate in contact with the residual *gaseous phase*.

This last case is the one which has given rise up till now to the most important investigations. We will suppose not only that the liquid remains constantly and wholly in contact with the gases from which it is derived, but that this contact is *altogether intimate* and perfect, through the agitation of the recipient where liquefaction is accomplished, or this recipient, which is generally a closed and almost capillary Cailletet tube, through the agitation in the body of the liquid itself of a small soft iron cylinder controlled by an external magnet—an elegant device invented by Kuenen.

Under these conditions, there is manifestly equilibrium at each moment between the tension of the vapour of the liquid—that is, the elastic force of the vapours composing the gaseous phase—and the pressure of liquefaction. Since the latter augments regularly as liquefaction proceeds, it consequently implies that the tension of the vapour of the liquid, *although at constant temperature* in each of the experiments, *increases* also in a continuous fashion instead of remaining constant as is the case with simple gases.

Before deducing from this fact the interesting consequences it involves, let us make an important remark.

Let us take a gaseous mixture of this character which is partially liquefied under the influence of a suitable temperature and pressure (the reasoning is applicable to all cases, even to the temperatures of the critical zone). Owing to the presumed intimate contact between liquid and gas, there is complete equilibrium between the two

phases; the liquid and the gas have mutually exchanged all they could at this temperature, and the atmosphere is *saturated* with the liquid, on the same footing that salt water is saturated when covering an excess of non-dissolved salt. Its composition is the result of the saturation itself. If, therefore, we increase the gaseous phase by the addition of a certain quantity of a gaseous mixture of perfectly identical composition, pressure and temperature, that is equally saturated, this addition will manifestly have no effect on the liquid, for the same reason that if we added to the salt water above mentioned a fresh quantity of saturated salt water the non-dissolved salt would not be affected.

For an identical reason, the liquid phase would in no respect be changed if we were to remove any part whatever of the gaseous phase.

We should similarly find that without in any way changing the gaseous phase, we could withdraw all or any part of the liquid phase, or, on the contrary, add thereto liquid of the same composition and same temperature.\*

This signifies that—

(1) When we liquefy progressively such a gaseous mixture at constant temperature lower than the temperatures of the critical region, the liquid formed *does not present*, as we might think, *a constant composition* identical with that of the gaseous mixture; for if this were the case, the tension of the liquid at the constant temperature of the experiment would have no reason for varying, and the liquefaction, as was the case with a simple fluid, would be accomplished entirely at constant pressure—which is not the case.

(2) The liquefaction is not divisible—as one might also imagine—into two distinct phases, the first comprising

\* The above reasoning is not always applicable to the mixtures of very close gases, because it is possible that conditions of indifferent equilibrium might intervene between liquid and gas. This is one of the reasons for the restrictions laid down above.

the liquefaction, partial or entire, of the element  $L$  only. Let us, in fact, suppose that this is the case, and that when  $L$  is perfectly liquefied, we avail ourselves of the right which we have recognised we possess of withdrawing all or a portion of the gaseous phase without affecting the liquid. Let us reduce this liquid phase to zero. We have only the liquid left, which ex-hypothesis is constituted solely of the element  $L$ . The pressure of the system is manifestly then equal to the tension  $p$  of liquid  $L$  at the temperature in question, and this should be consequently also the pressure of liquefaction, since we have changed nothing either in the pressure or the temperature. Therefore as this reasoning varies for any given moment of the supposed condensation of  $L$ , the liquefaction is carried out during all this period under the constant pressure  $p$ —which is impossible.

(3) The continual variation of the tension of the liquid at the constant temperature of the experiment reveals, on the contrary, *a continuous variation in the composition of the liquid*, proportionate to the progress of liquefaction.

This variation in tension evidently, on the other hand, being affected in the direction of increase, necessitates that the composition of the liquid phase should be constantly *diminishing*, because the increase of the proportion of the element  $V$  in the liquid furnishes the necessary and obvious reason for the progressive increase of the tension.\*

In its continual decrease, the composition of the liquid phase tends necessarily towards the composition itself of the initial mixture which is attained when total liquefaction takes place. It is manifest, in accordance with this, that during the whole course of liquefaction the composition of the liquid remains *superior* to the initial composition, and *à fortiori* to that of the gaseous residue, but that the latter,

\* This amounts to saying that in progressive liquefaction, the more liquefiable element condenses preferentially in the first portion. We shall see (following chapter) the advantage taken by Claude of this fact in solving the problem of the separation of the elements of the air.

as compensation, must remain constantly *inferior* to the composition of initial mixture.

All these facts are in complete opposition to Dewar's conclusions, and this arises, we must repeat, from the circumstance that this scientist had not effectively placed himself in the conditions of partial liquefaction of the totality of the air he dealt with.

(4) If the composition of the liquid continues thus diminishing from the first drop, we nevertheless know nothing of its initial composition, and we may ask ourselves whether this might not be constituted *exclusively* of the element  $L$ . Now this is impossible, for if it were so, the reasoning in the second paragraph applied to this first drop of liquid shows that the liquefaction, whatever its composition, *would always start* for  $L$  from a pressure equal to the tension  $p$ , at the temperature under consideration; but this would be impossible, because a mixture  $A$ , partially liquefied at the cost of pressure starting *ex-hypothesis* from  $p$  and progressively increased up to  $P$ , and then separated from its liquid, furnishes a gaseous mixture  $B$  of inferior composition, whose first drop *will manifestly not be formed at  $p$* , but at  $P$ .

Thus the first drop cannot itself be formed exclusively of  $L$ ; it must include also  $V$ .

For example at  $67^{\circ}$  C. the mixture 26 per cent.  $\text{SO}_2$  and 74 per cent.  $\text{CO}_2$  yields a first drop containing 62 per cent.  $\text{SO}_2$ .

(5) The above reasoning, applicable to any mixture *whatever*, demonstrates also that the initial pressure of liquefaction *is always superior to  $p$* , always superior to the pressure of liquefaction of the more condensable constituent. This fact is manifestly due to the presence of  $V$  in the first drop.

For example, the above mixture has its dew-point at 58 atmospheres, against 13 atmospheres only in the case of  $\text{SO}_2$  at the same temperature.

In this way, therefore, the first drop itself furnished by a mixture cannot be formed of the more liquefiable constituent alone. A very remarkable fact—this first drop already involves a certain proportion of the *more volatile element*, however refractory this may be to liquefaction, and this at temperatures which may immeasurably exceed its *critical temperature*.

In this way, according to Andrews,\* the mixture  $6 \text{ CO}_2 + 1 \text{ N}$  commences to liquefy under the pressure of 48.3 atmospheres at the temperature of  $+3.5^\circ \text{C.}$ , which is enormously distant from the critical temperature of nitrogen  $-146^\circ \text{C.}$ , and that nevertheless this first drop contains a notable proportion of nitrogen. At 102 atmospheres, the whole mixture is in the liquid state.

Better still :

According to Cailletet, hydrogen, which is so refractory to liquefaction that its critical temperature has to be sought at  $-242^\circ \text{C.}$ , is susceptible, when it is mixed with a high proportion of carbonic acid, of being partly liquefied at the ordinary temperature of the atmosphere.

We see to what a profound upsetting in the case of these mixtures our notion of the critical temperature (p. 50) is exposed†, and how much we should err in supposing that to avoid the liquefaction of the more volatile constituent of a mixture it would be sufficient to operate below the critical point of this element and inversely. The individual properties of gases thus appear to be profoundly altered in gaseous mixtures. The reason is that it is wholly erroneous to consider a gaseous mixture as constituted by two elements perfectly independent of each other and both of them preserving their proper individuality, each of them behaving on liquefaction as if it were isolated, and subjected to a reduced pressure corresponding to its propor-

\* Posthumous memoir of Andrews, presented by Stokes to Royal Society, March 18th, 1886.

† As Claude effected this in a patent mentioned above (p. 334).

tion in the gaseous mixture. This conception, to which Dalton's law has habituated us in the matter of the solution of gases, is wholly erroneous in the matter of liquefaction, as in a sense we have to deal then with new entities.

(6) Suppose a mixture  $A$  of constitution  $a$ . At the dew-point, under a pressure  $P$ , intermediate, according to paragraph (5), between the liquefaction pressures of the two constituents, this yields, according to paragraph (3), a liquid of the composition  $\beta > a$ .

Let us advance the liquefaction by increasing the pressure. The composition of the liquid, according to paragraph (3), diminishes progressively, and under a pressure  $P_1 > P$  attains a composition  $\beta_1 < \beta$ , besides, according to paragraph (3), last portion,  $a_1 < a$ ,  $a_1$  being the composition of the gaseous residue.

Now, in accordance with our habitual practice, let us remove the liquid phase; there remains thus a second gaseous mixture  $A_1$  of lower composition  $a_1 < a$ , which is manifestly at its dew-point, and which would give us thus at a pressure  $P_1$  higher than  $P$  a first liquid drop of lower constitution  $\beta_1 < \beta$ .

Thus liquefaction commences at a pressure intermediate to those which would bring about the liquefaction of the isolated constituents, and which is *all the higher* at the selected temperature that the % constitution of the mixture is lower; this furnishes a liquid whose initial constitution, always lower than 100 per cent., but always higher than that of the mixture, is *all the lower* the lower is the % constitution of the mixture itself, and diminishes progressively down to this constitution in the course of liquefaction. For example, the mixture  $CO_2 + SO_2$  of the constitution 38 per cent.  $CO_2$  commences to liquefy at  $70^\circ$  C. under 45 atmospheres, yielding 82 per cent., while the 25 per cent. mixture only commences to liquefy at 66 atmospheres and yields initially 56 per cent.

(7) We are now fixed on the initial and final composition of the liquid; the initial composition of the gaseous phase is equally known to us. There only remains for us to study the final composition of this gaseous phase, that is, the composition of the last gaseous bubble, and the question does not lack interest because we can ask ourselves if, owing to the antecedent liquefaction of  $L$ , this last bubble may not be composed exclusively of  $V$ .

Now suppose that is so. Let us increase the gaseous phase by adding gas of the same composition—that is, composed of pure  $V$ ; we shall thus form a system (liquid + gas) capable of achieving its liquefaction under constant pressure, which is contrary to experience.

Therefore, just as the first liquid drop already contains the element  $V$ , the last gaseous bubble still comprises the element  $L$ . It is even so, and the fact is of capital importance in the oxygen industry, that the progressive liquefaction of the air at  $-190^{\circ}\text{C}$ . in contact with the liquid produced is completed under 1 atmosphere pressure with a gaseous residuum still containing 1 per cent. oxygen.

We should remark that the respective proportions of  $L$  and  $V$  in the gaseous phase are manifestly ruled by the individual tensions of  $L$  and  $V$  in the liquid phase, but the individual tensions, instead of being constant at the selected temperature like that of  $L$  alone or of  $V$  alone, depend essentially on the respective proportions of  $L$  and  $V$ . This is one of the consequences of the law of mass. If  $L$  largely predominates, its proper tension represents almost the total tension of the liquid; the composition of the gaseous phase is therefore high, although inferior to that of the liquid, and the pressure of the system does not largely surpass the liquefying pressure of  $L$  alone; thus the initial stage of the liquefaction of a gaseous mixture rich in  $L$  is, so to speak, dictated by the aptitude for liquefaction of  $L$  alone, the presence of  $V$ , which remains preferentially in the gaseous residuum, acting principally upon the final stages.



If  $V$ , on the contrary, largely predominates, its proper tension represents almost the whole of the entire tension, which, on the other hand, is much higher than in the preceding case at the same temperature; the proportion of  $V$  in the gaseous phase is therefore very high; at dew pressure, which is a little lower, we barely suspect the influence of  $L$ , and the boiling pressure is almost as high as for  $V$  alone. We shall see with what suggestive clearness these facts show themselves when we shall have learned to represent them by curves.

We must still point out an exceedingly remarkable property which the preceding considerations have already made us suspect.

Consider a separate mixture, under the effect of a convenient temperature  $T$  and pressure  $P$ , in a gaseous phase of composition  $\alpha$ , and a liquid phase of higher composition  $\beta$ . Without altering the equilibrium, we can diminish indefinitely the liquid phase. We can also increase it indefinitely. We thus form systems whose comprehensive composition (liquid + gas) is decreasing down to  $\alpha$  in the first case, and increasing up to  $\beta$  in the second case.

We thus immediately see that in all cases the mixtures whose composition is comprised between  $\alpha$  and  $\beta$  furnish at temperature  $T$  and pressure  $P$ , a gaseous phase of the same composition as  $\alpha$ , and a liquid phase of the same composition as  $\beta$ . The relative proportions of these two phases alone change, the mixture, whose limit is of the composition  $\beta$ , being exactly liquefied, that is, possesses its boiling-point at  $(TP)$ , and the mixture  $\alpha$  possesses, on the contrary, its dew-point thereat. As to mixtures superior to  $\beta$ , they are wholly liquefied under the conditions  $(TP)$ ; while those inferior to  $\alpha$  remain wholly gaseous.

Thus, for all the mixtures of  $L$  and  $V$ , capable of yielding at the temperature  $T$  and the pressure  $P$  a liquid

phase and a gaseous phase, the composition of each of these phases is *absolutely invariable*, and independent of the composition of the mixture.

**Duhem's diagram and its application to the determination of concomitant compositions.**—The very interesting property which we have just put in evidence has been demonstrated from a much more general point of view by Gibbs. The profound corresponding member of the institute, Duhem, deduced therefrom a most important consequence, which is derived directly from the very

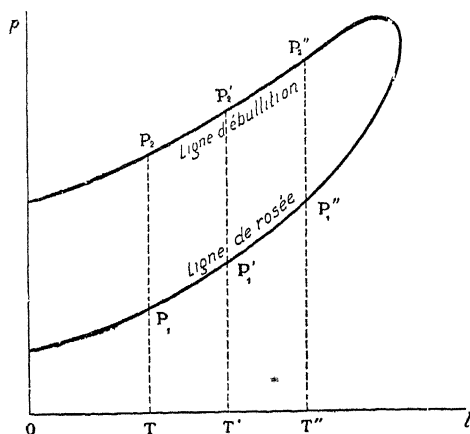


FIG. 123.—Duhem's graphical representation.

simple graphical mode of representation devised by him. In Fig. 123 the temperatures are the abscissæ, the pressures are the ordnates. The mixture investigated, brought to a constant temperature  $T$  compatible with its liquefaction, is submitted to the action of a progressively increasing pressure. At the pressure  $P_1$  a first drop of liquid appears. This is the dew-point. The pressure still increases; the amount liquefied augments more and more. At  $P_2$  it is complete: this is boiling-point.

If we renew the same experiment with the same mixture, but for a complete series of different temperatures,

we get a succession of dew-points  $P_1, P_1', P_1''$ ,—which mark a regular curve  $P_1, P_1''$ , called by Duhem *the dew-line*, and a succession of boiling-points  $P_2, P_2', P_2''$ —which compose in the same way the *line of ebullition*  $P_2 P_2''$ .

Owing to certain remarkable circumstances, but on which we are unable to insist here, these two lines unite in a perfect manner, and constitute in reality a single curve, which comprises not only the total zone of liquefaction, but also the critical zone, in spite of the strange peculiarities thereof. The curve which we have just constructed gives a complete history of the liquefaction of a given mixture; but for each mixture of the two same gases, or at least for a suitable succession of graduated mixtures, it is possible to construct a similar curve. We then obtain a general result, an example of which is given in Fig. 124, which summarises the experiments of Caubet on the mixtures of  $SO_2 + CO_2$  of the following compositions :

		$SO_2$ .	$CO_2$ .
Mixture No. 1	. . .	0.0732	0.9268
„ 2	. . .	0.1129	0.8871
„ 3	. . .	0.2542	0.7458
„ 4	. . .	0.3787	0.6213
„ 5	. . .	0.5063	0.4937
„ 6	. . .	0.6255	0.3745
„ 7	. . .	0.7495	0.2505
„ 8	. . .	0.8750	0.1250

The figure is completed on one side by the curve of vapour tensions of pure carbonic acid, and on the other by that of pure sulphurous acid.

Taken by itself, the general appearance of this assembly is already very instructive. It shows at once the influence of the more condensable gas on the *commencement* of liquefaction through the manifest affinity of the dew lines with the curve of liquefaction I of this gas, affinity more and more noticeable in proportion to the increased proportion

of this element; it shows, on the contrary, and in a no less striking fashion, the affinity of the lines of ebullition, with

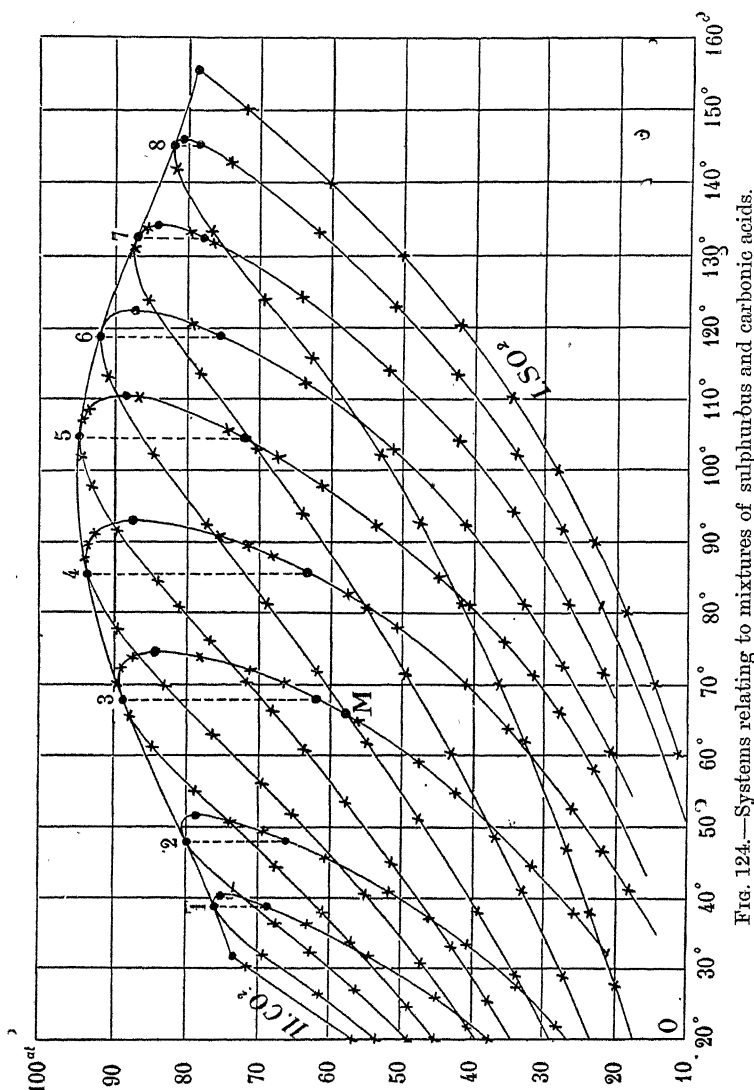


Fig. 124.—Systems relating to mixtures of sulphuric and carbonic acids.

the curve of liquefaction II, and, consequently, the influence of the less condensable gas upon the end of liquefaction.

Let us now consider any mixture whatever, and let us suppose that at the temperature of 66.3° C. and a pressure

of 57.6 atmospheres, for example, the said mixture is capable of existing partially in the liquid state. What are the respective compositions of the gaseous phase and the liquid phase? We know already that at this temperature and at this pressure the composition of the liquid and that of the gas are perfectly determinate, and do not at all depend upon the general composition of the mixture under consideration.

As the gaseous phase does not alter if we remove the liquid phase, it is manifestly identical in composition *with the mixture which has its dew point at M*, and, by referring to the figure, we see that it is mixture No. 3 which satisfies this condition.

Similarly, the liquid phase, remaining unmodified if we remove the gaseous phase, is necessarily identical in composition *with the mixture which has its boiling-point at this point M* (66.3° C., 57.6 atmospheres), and we see on the figure that it is mixture No. 6 which responds to this condition; therefore, for all mixtures capable of furnishing at 66.5° C. and 57.6 atmospheres liquid phase and a gaseous phase, the proportion of SO<sub>2</sub> in the liquid phase will be compulsorily that of mixture No. 6, that is, 62.5 per cent., and the proportion of the gaseous phase will be that of mixture No. 3, viz. 25.4 per cent.

It is evident otherwise that if, instead of studying certain mixtures, we had experimented on an infinitude, we should have obtained an infinitude of curves immeasurably slightly separated one from another, so that at each point of the surface limited by the curves I and II a dew line and a line of ebullition which it is more easy to delineate by comparison with neighbouring lines must intersect. Duhem's remarkable theorem amounts therefore to saying that, if a mixture is susceptible of being partially in the liquid state at a certain temperature  $T$  and under a certain pressure  $P$ , *its two phases have respectively the composition*

of the two mixtures whose lines of dew points and ebullition cut at the point *TP*.

From which several interesting consequences arise:

(1) The dew line in question, in accordance with the form of the curves, necessarily belongs to a mixture of

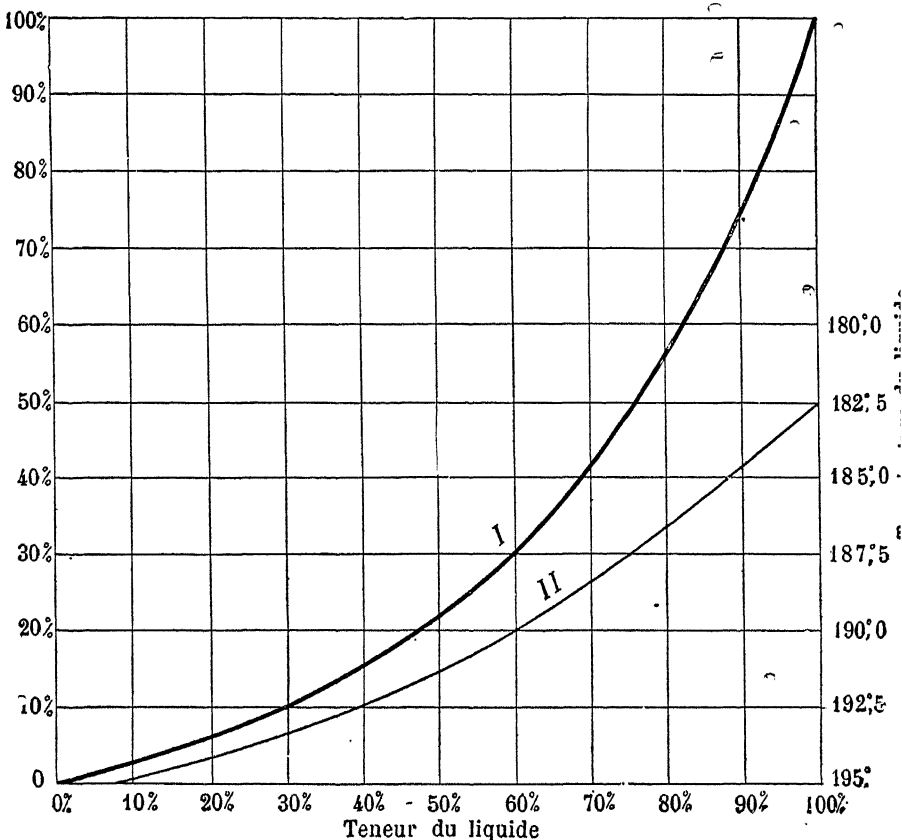


FIG. 125.

considerably inferior composition than that of the ebullition line; such as, for example, composition No. 4 or 38 per cent.  $\text{SO}_2$ , for the gaseous phase of the point (55 atmospheres,  $81^\circ \text{C.}$ ), as compared with composition No. 7 or 75 per cent.  $\text{SO}_2$  for the liquid phase at this same point. This confirms what we already know, viz. that a partial

liquefaction always condenses preferentially but not exclusively the more volatile component.

(2) The above system, relating to different mixtures of two gases, having been constructed once and for all by a series of preliminary experiments—which, be it remarked, once the mixtures are made, only include the manometer and thermometer readings—it is possible to determine at once, without the necessity of any sampling or analysis, the concomitant composition of a mixture equally indefinite, provided we only know the temperature and the pressure. Here is manifestly a much more elegant method, and capable of more general results than the direct method, consisting of taking simultaneous samples of the liquid and the gas directly for the purpose of analysis, such as we have seen Baly do.

It is highly regrettable, so far as we are concerned, that the systems for the mixtures of oxygen and nitrogen have not yet been constructed.

(3) A given line of ebullition cuts successively *from right to left* all the dew lines corresponding with more and more poor mixtures. This means that the more we effect liquefaction at low temperatures, and, therefore, the more we work under light pressures, the more the composition of the concomitant phases differ, the *better* the antecedent liquefaction of the less volatile component is accomplished. This is an interesting indication for the process which we are going to describe under the title of *backward return*.

Nevertheless the way in which the concomitant compositions diverge one from the other depends essentially on the form of the curves of the gaseous mixture under consideration. These few examples show sufficiently all the services which the systems thus constructed can render, and we must reiterate our regret that that of the mixtures of oxygen and nitrogen is still unknown.

## CHAPTER XVII

### APPLICATION OF ANTECEDENT LIQUEFACTION OF THE OXYGEN OF THE AIR

It is now, we believe, wholly agreed that, when a mass of air is subjected in a homologous way to a temperature capable of maintaining a portion thereof in the liquid state, and that a sufficiently intimate contact exists between the two phases, the respective composition of the two phases is exactly determined: it matters little in this connection that these two phases are the result of the partial condensation of gaseous air, or, on the contrary, of the partial evaporation of the liquid air. Thus the fact pointed out by Claude in his note of 1903 to the Academy is definitely established; the curve which we have just now indicated (p. 304) as furnishing all the peculiarities of the evaporation of liquid air—Baly's curve—is equally applicable to liquefaction, and can with the same exactness foretell all its peculiarities.

**Examples.**—So that liquid air which is evaporating should furnish gas of the composition of atmospheric air, viz. 21 per cent., it must, according to the curve, be itself of the proportion of 47 per cent. Well, inversely, if atmospheric air, air of 21 per cent. is made to progressively liquefy, the first drop which is formed will be composed of very rich liquid, testing precisely 47 per cent.

More generally still—and this is very important—if some liquid air and some gaseous air of any reciprocal composition are placed in sufficiently intimate contact, there is established between them very rapidly, an exchange such as



in the final composition A in the liquid, responds in the gas to the corresponding composition B—always becoming more feeble—indicated by the curve. Experience verifies completely all these forecasts of theory. For example, a liquid of 21 per cent. can only subsist normally with a gas of 7 per

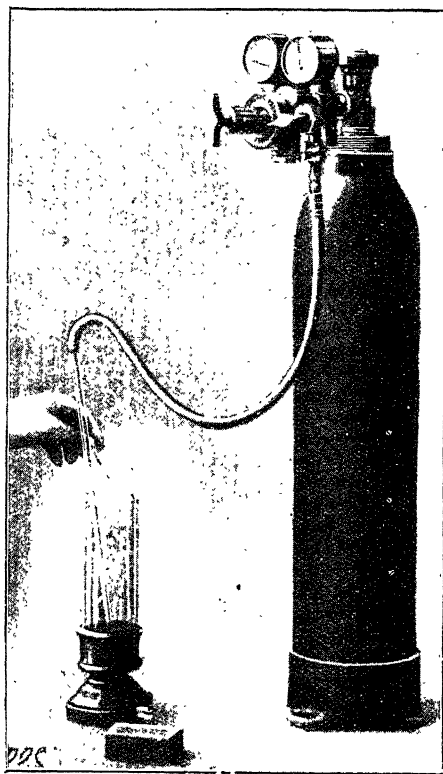


FIG. 126.—Transformation of oxygen into nitrogen in the course of rising through liquid air.

cent., a liquid of 47 per cent. with a gas of 21 per cent., and so on. In other words, the liquid is only in normal equilibrium, in stable equilibrium, with a gas, precisely identical with that which it would itself furnish when evaporating.

Now if we seek for a deep reason for this fact, we have no difficulty in finding it in the more or less low

temperature of the liquid air as a function of its composition: if the liquid in contact with the gas contains more nitrogen than is indicated by the concomitant composition, it is therefore too cold, and condenses a portion of the gaseous oxygen in the place of a part of the nitrogen which evaporates. If it contains too much oxygen, the contrary takes place; this second case is at the first blush more strange than the preceding, because it seems extraordinary that the nitrogen can be liquefied while bringing about the evaporation of the less volatile oxygen. But we must not forget that if for each temperature oxygen and nitrogen possess individual tensions whose sum counterbalances the external pressure, these tensions, which by their ratio exactly determine the respective proportion of the two constituents of the evaporated gas, depend, not only on the temperature, but also (p. 348) *on the degree of dilution* of this constituent of the mixture: it is because the tension of the nitrogen in the liquid air, rich in oxygen, is attenuated by dilution, in spite of the more elevated temperature, that this rich liquid air is capable of condensing nitrogen against oxygen in spite of the individual volatilities of these two gases.

It is easy to throw the light of a convincing experiment on this important point (Fig. 126).

Here is a tube through which pure oxygen is discharged. We plunge it into this test-tube filled with liquid air. The oxygen is given off in bubbles through the liquid, but when these bubbles reach the surface, they extinguish this lighted match! And, in point of fact, surrounded on every side by liquid at the temperature of  $-193.5^{\circ}\text{C.}$ , the oxygen of the bubbles, which individually liquefies at  $-182.5^{\circ}\text{C.}$ , is progressively condensed in the course of its ascension, and has been progressively replaced by the more volatile nitrogen to the proportion of 7 per cent., which, according to the diagram, corresponds to a liquid of

21 per cent. Thus it was the oxygen which arrived at the bottom of the liquid; while it is almost pure nitrogen which reaches the surface, and we have seen that the match did not err.

The reverse experiment, much more paradoxical in appearance, succeeds equally well for the reasons we have just indicated, that is, because pure nitrogen arising in bubbles in the liquid oxygen, is progressively condensed in

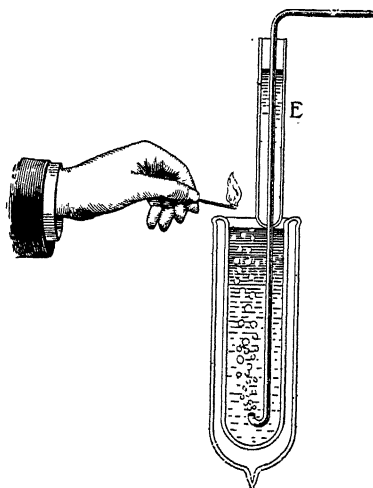


FIG. 127.—Transformation of nitrogen into oxygen in the course of its ascension through liquid oxygen.

the course of its upward journey so that the bubbles reach the surface in the condition of oxygen.

To avoid all error in the interpretation of this extraordinary experiment, it is well that the nitrogen should reach the lower portion of the liquid oxygen thoroughly cooled, so that it is impossible to place the result obtained to the account of the partial evaporation of the oxygen at the expense of the heat of cooling. Fig. 127 indicates the means of realising this *desideratum*.

We must now take advantage of the knowledge which we have just gained, and to start with, of the antecedent liquefaction of the oxygen.

There is some difficulty in doing this, for this antecedent liquefaction cannot be advantageously utilised if it does not lead to the separation in a pure condition of all or a part of the nitrogen; and it does not seem *à priori* that this can be so, since in the preceding theoretical conditions we have shown that even at the end of progressive liquefaction, the gaseous residue still contains a certain proportion of the less volatile constituent.

Let us suppose, for instance—and it is about on these lines that Le Sueur works in the first patent where, after Ramsey, the idea of the antecedent liquefaction of oxygen is again taken up\*—suppose that we content ourselves with separating the air by partial liquefaction into a portion rich in oxygen, and a gaseous residue in equilibrium with this liquid mass. This latter fraction, although much less rich in oxygen, still contains a good deal of it, as appears even from Baly's diagrams. The calculation is easy. If we reduce 100 parts of air of 21 per cent. to the liquid phase  $(100 - x)$  of the composition of  $y$  liquid in equilibrium with a gaseous phase  $x$  of the composition of  $y$  gas, we shall obviously have:

$$xy \text{ gas} + (100-x) y \text{ liquid} = 21.$$

Furthermore,  $y$  liquid and  $y$  gas must be of co-existing composition, which permits, as shown by Baly's results, of obtaining by successive approximations the values of  $y$  liquid and of  $y$  gas corresponding to  $x$ .

For example, let us take  $x = 80$ , and suppose  $y$  liquid = 30 per cent. We have then, according to Baly,  $y$  gas = 10 per cent., and—

$$80 \times 0.10 + 20 \times 0.30 = 14, \text{ and not } 21.$$

Therefore, 30 per cent. and 10 per cent. are too small values for  $y$  liquid and  $y$  gas. The true values are  $y$  liquid = 41 per cent., and  $y$  gas = 16 per cent., for—

$$80 \times 0.16 + 20 \times 0.41 = 21.$$

\* Canadian patent No. 74430.

We thus obtain the following table :

$x$ .	$y$ Gas.	$y$ Liquid.	Amount of condensed oxygen.	Percentage of condensed oxygen.
100	21.0	47	0.0	0
80	16.0	41	3.2	39
60	12.5	34	13.6	65
40	9.5	28	16.8	80
20	8.0	24	19.2	91
0	7.0	21	21.0	100

The results are represented by the curves I, II, III, (Fig. 128).

If, for example, we should stop at a gaseous residuum,  $x = 60$ , this residuum, which we should be led to reject since it only tests 12.5 per cent., contains 7.5 parts of oxygen out of 21, that is, a loss equal to one third before any evaporation.

We may therefore say that the partial separation thus realised through antecedent liquefaction is dearly paid for, and that, applied under such conditions, this antecedent liquefaction would be of no use. We are, however, going to see what considerable service Claude was able to obtain from it in combination with the phenomena of rectification.

We commenced by remarking that we could already obtain a better result than the preceding if, instead of leaving the liquid progressively formed in intimate and continuous contact with the residual gas, as we have constantly premised till now, it was withdrawn as and when formed.

The operation would then correspond exactly to the inverse of progressive evaporation whose results are represented by Linde's diagram (Fig. 110), and in which it was the gas formed which was withdrawn when formed: and we can here construct with the tests of the liquid formed a curve II (Fig. 129), which will have the same

signification as the curve of gas formed (Fig. 110); the area subtended by curve II, starting from the beginning of the operation, that is, from the right-hand side of the figure, will be at each instant equal to the quantity of oxygen condensed with the liquid. The total area must,

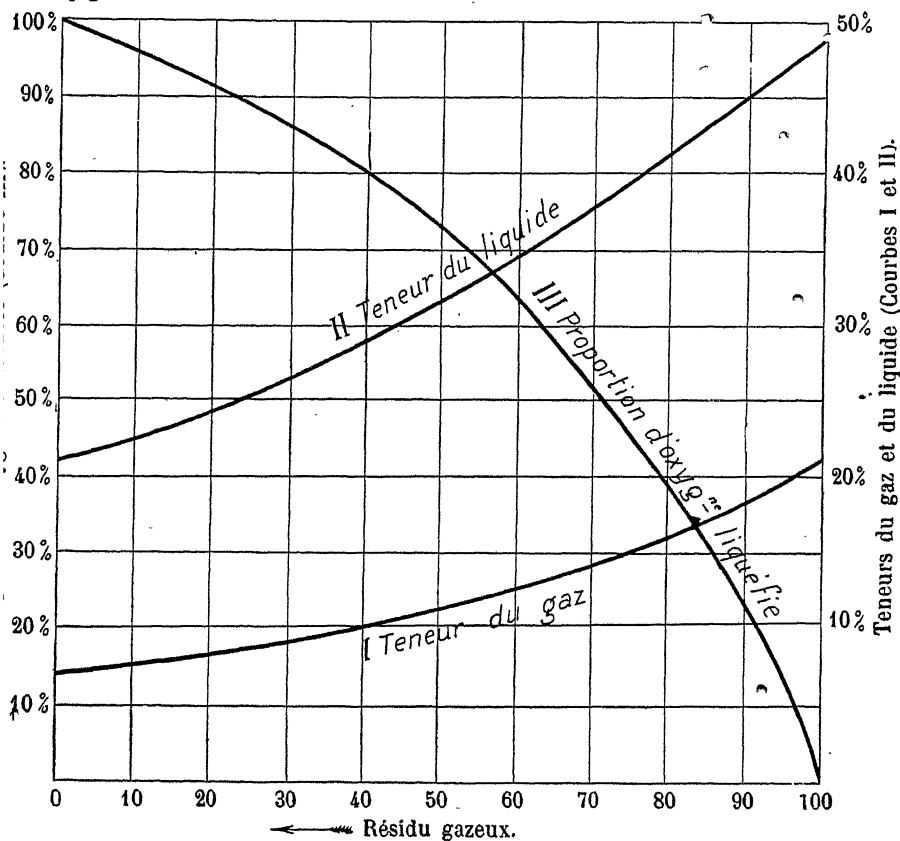


FIG. 128.—Progressive liquefaction of the air, the gaseous phase remaining in contact with the liquid phase.

consequently, be equal to the surface below the line of 21 per cent., which represents the total oxygen contained in 100 parts of air.

It is manifest that in this conception the impoverishing of the gaseous residuum is much more rapid, since for the same quantity of liquid formed the gaseous constituent MP is

tied here to the *final* constitution NP of the liquid at  $x$ , and no longer to its *average* constitution, which is evidently stronger.

We calculate the curves, observing that  $y$  gas at each

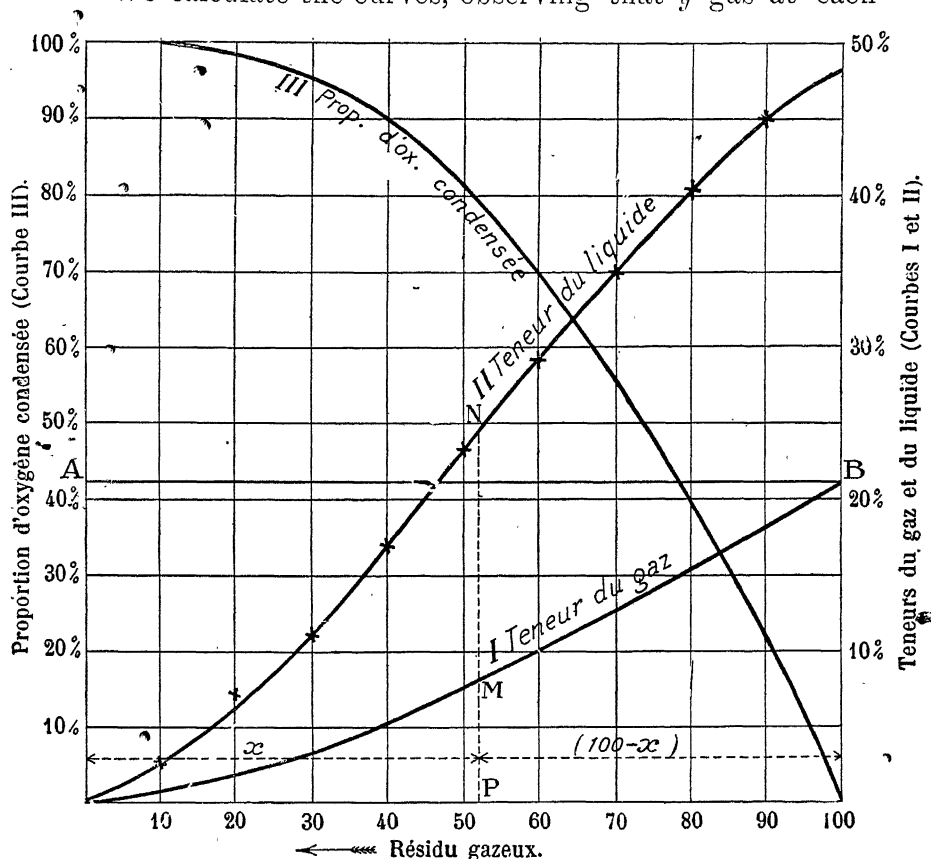


FIG. 129.—Progressive liquefaction of the air, the liquid phase being withdrawn as and when formed the composition of the gaseous phase already falls much more rapidly than in Fig. 128.

point equals the average ordinate of curve II from this point up to the end of condensation :

$$y \text{ gas} = \frac{21 - \text{quantity already condensed.}}{100 - x}.$$

Furthermore,  $y$  gas and  $y$  liquid must, as always, be of concomitant composition,

Making our calculations by tenths, which gives us a sufficient approximation, we obtain the following table :

$x$ Gaseous residuum.	$y$ Gas.	$y$ Liquid.	Amount of oxygen condensed and withdrawn.	Proportion of oxygen condensed.
100	21.0	47	0.0	0
90	18.0	45	4.5	21
80	15.5	40	8.5	40
70	12.5	34	11.9	57
60	10.5	29	14.8	70
50	7.5	24	17.2	82
40	5.0	17	18.9	90
30	3.5	11	20	95
20	2.0	8	20.8	99
10	0.5	2	21.6	100
0	0.0	0	"	"

Fig. 129, which represents these results, shows that the gaseous constitution (curve I) descends in this case to 0, although this result, according to theory (Chapter XVI), was wholly impossible when the liquid remained in contact with the gas, and that the gaseous constitution did not then descend effectively save to the limiting composition of 7 per cent.\* Thus in this case with the progressive elimination of the liquid we can attain to *pure nitrogen*, in the same way that we attain to *pure oxygen* in the inverse phenomenon of evaporation.

Nevertheless, in one and the other case it is only at the end of the operation that we attain to a pure constituent—nitrogen in the present case. If no added effect intervened we should therefore, in this case, have to again liquefy almost entirely to obtain a gaseous residuum sensibly free from oxygen, and consequently a separation of some utility.

**Backward return (1902).**—The conditions are entirely

\* Curve II, which results from these calculations, presents a form which is certainly inexact, as the surface comprised between this curve and the line A B 21 per cent., to the right of its intersection therewith, is not equal to the surface comprised between these same two lines to the left of their intersection as is required. This inexactitude is doubtless due to a slight imperfection in Baly's results.



changed in the following device, which Claude has styled a device *by way of backward return*, and which constitutes the basis of his processes for the extraction of oxygen, as expansion with external work is the basis of his processes for the production of liquid air. Let us consider the bundle of tubes *r*, immersed in liquid air contained in *v* (Fig. 130). At first sight this device recalls strongly that delineated previously (Fig. 112). It will, however, be remarked that the air to be treated, compressed, as usual, to some atmospheres' pressure, arrives at the bottom of the bundle of tubes, and not any longer at the upper part, where, on the contrary, is placed an orifice for the evacuation of the gaseous residuum.

Let us examine what profound modifications this simple variation implies in the working of the system.

As soon as it reaches the lower part of the bundle through *r*, the air to be treated, which is compressed and cold, commences to liquefy, but—as we now know—these first liquid drops test 47 per cent. Impoverished by this circumstance, the air rises in the bundle of tubes, and the liquid formed therein, though not testing any longer quite 47 per cent., is impoverished further through its formation of the residual gas, which will in turn yield a little higher up a liquid that is a little poorer, and so on. Finally, close to the top of the bundle the gaseous residuum will be composed of approximately pure nitrogen.

We find here, practically realised, the method of the progressive liquefaction of the air, with continual elimination of the liquid which we have been studying, and we can only repeat what we have said—that is, that if no added effect intervened, it would even in this case be only through an almost total liquefaction that we should reach practically pure nitrogen.

Very luckily, through the arrangement of the circumstances themselves, a capital fact is brought into play.

Making our calculations by tenths, which gives us sufficient approximation, we obtain the following table :

$x$ Gaseous residuum.	$y$ Gas.	$y$ Liquid.	Amount of oxygen condensed and withdrawn.	Proportion of oxygen condensed.
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60	10.5	29	14.8	70
50	7.5	24	17.2	82
40	5.0	17	18.9	90
30	3.5	11	20	95
20	2.0	8	20.8	99
10	0.5	2	21.6	100
0	0.0	0	"	"

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Let us examine what profound modifications this simple variation implies in the working of the system.

As soon as it reaches the lower part of the bundle through *t*, the air to be treated, which is compressed and cold, commences to liquefy, but—as we now know—these first liquid drops test 47 per cent. Impoverished by this circumstance, the air rises in the bundle of tubes, and the liquid formed therein, though not testing any longer quite 47 per cent., is impoverished further through its formation of the residual gas, which will in turn yield a little higher up a liquid that is a little poorer, and so on. Finally, close to the top of the bundle the gaseous residuum will be composed of approximately pure nitrogen.

We find here, practically realised, the method of the progressive liquefaction of the air, with continual elimination of the liquid which we have been studying, and we can only repeat what we have said—that is, that if no added effect intervened, it would even in this case be only through an almost total liquefaction that we should reach practically pure nitrogen.

Very luckily, through the arrangement of the circumstances themselves, a capital fact is brought into play.

In proportion as the liquid air is produced it falls back owing to its weight in the reverse direction to the rising gases.

This is the *backward return*.

It thereupon comes in contact with gases which are progressively richer than those from which it originated. Now, in accordance with what has been explained, equilibrium is impossible between these gases and this liquid, which is too cold compared with them, on account of its

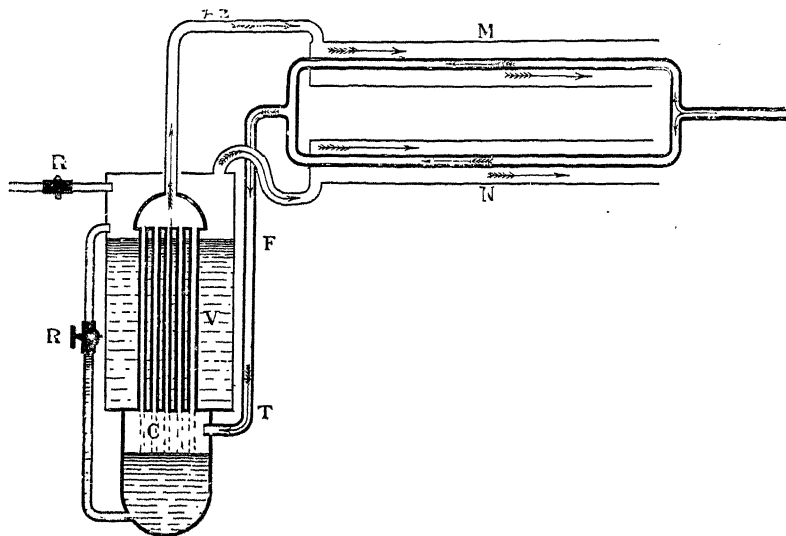


FIG. 130.—Partial liquefaction by backward return.

excessive proportion of nitrogen. A portion of the more condensable oxygen of the gaseous mixture thereupon condenses and takes the place in the liquid of the nitrogen which is evaporated.

The same phenomenon will be produced naturally in all the portions of the bundle which the oxygen can penetrate, so that on the whole the descending liquid will act in respect to the ascending gas like a cold shower bath, energetically condensing the oxygen and accelerating indefinitely the exhausting action of the progressive liquefaction.

On the whole, the liquid which is formed, comprising the whole of the oxygen, drains off at the bottom of the bundle with a composition which may reach 47 per cent.—for a reason which we are beginning to understand—while half of the air treated escapes at the upper part of the bundle, *in the condition of practically pure nitrogen without the necessity of being liquefied.*

The calculation of the curves is here easy, since in the theoretical case the test is constant and equal to 47 per cent. so long as the proportion which is liquefied is insufficient to carry off all the oxygen. We get, therefore, the following table :

$x$ Gaseous residue.	$y$ Gas.	$y$ Liquid.	Amount of oxygen condensed.	Proportion of oxygen condensed.
100	21	47	0.0	0
90	18	47	4.7	23
80	14.5	47	9.6	46
70	9	47	14.4	70
60	3	47	19.2	90
50	0	47	21.0	100

We see how essentially this table differs from the two preceding ones. Truly, we encounter here the limiting conditions; if we liquefy too much in the bundle of tubes, the non-liquefied nitrogen will issue very pure,\* but if it falls short, on the contrary, the liquid will flow off at the bottom of the bundle—with a test notably inferior to 47 per cent. If, on the contrary, we do not liquefy enough, the liquid will flow off at 47 per cent.—the extreme test which it can attain;† but, on the contrary, the nitrogen will carry off a notable proportion of oxygen. Be it noted that, from the point of view of purity of nitrogen, combined with ease of

\* Accompanied, however, by the rare slightly condensable gases of the air, neon and helium, which permits of devising a very interesting process for the preparation of these new bodies.

† Excepting the small disadvantageous modification which may result from the existence of pressure in the liquifier, in accordance with the note on p. 355.

In proportion as the liquid air is produced it falls back owing to its weight in the reverse direction to the rising gases.

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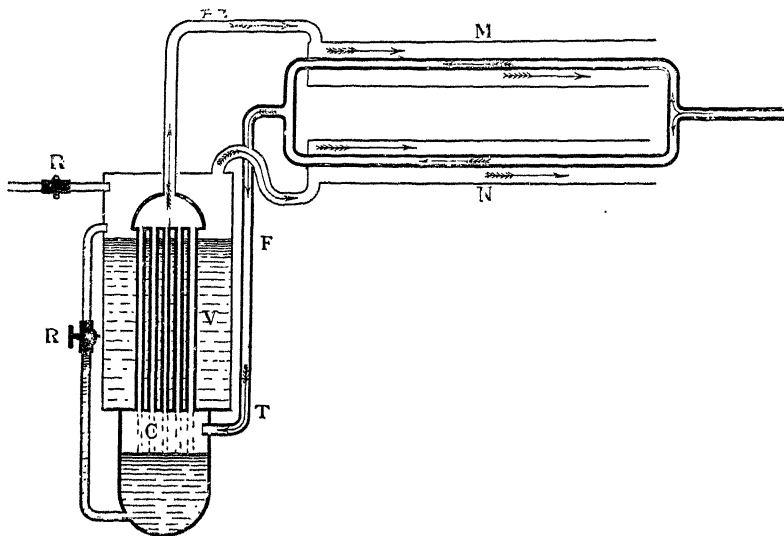


FIG. 130.—Partial liquefaction by backward return.

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† Excepting the small disadvantageous modification which may result from the existence of pressure in the liquifier, in accordance with the note on p. 355.

regulation, we may have considerable interest in placing ourselves in the first case, that of a slightly more abundant liquefaction than that corresponding with the exact separation into 47 per cent. and nitrogen. Moreover, the liquid

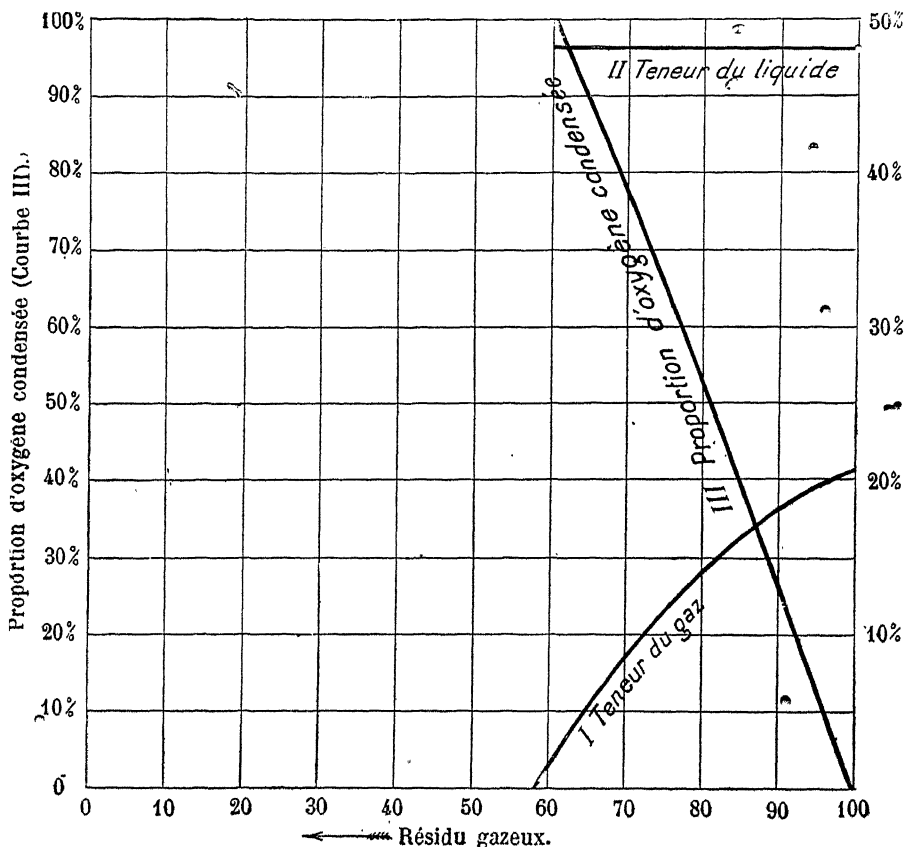


FIG. 131.—Rapid exhaustion of the gaseous phase in the case where the progressively liquefied air is withdrawn by backward return.

which is formed at the top of the bundle when the cycle is first established is capable of purifying the succeeding gases down to an inferior test to that of the preceding gases, hence a purifying action is set up which is *auto-progressive* and tends to energetically maintain the purity of the nitrogen,



and which we shall meet with again in use in other systems.

The separation thus achieved, thanks to the backward return, is effected with exceeding facility.

For example, Claude communicated to the Academy of Sciences\* the results of an experiment in which he

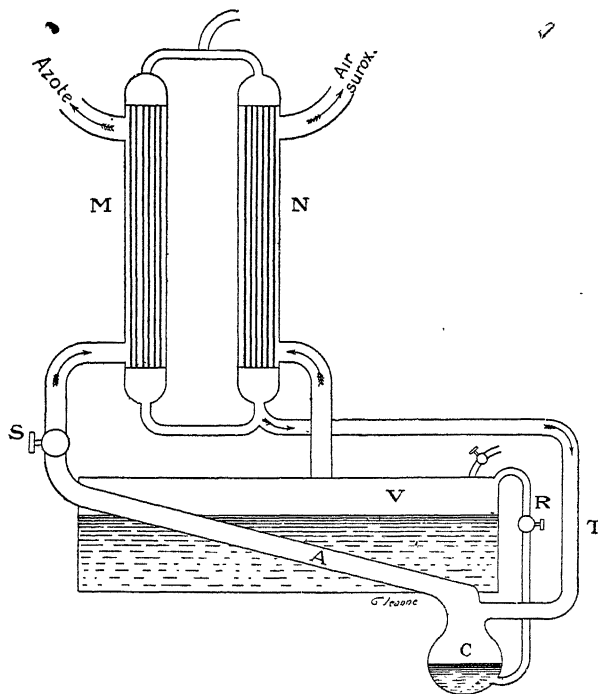


FIG. 132.—First realisation of the backward return.

utilised a bundle of pipes 12 millimetres in diameter and 2 metres in length. Well! while the liquid obtained at the bottom tested 50 per cent., the residual gas was composed of 98 per cent. nitrogen.

On the other hand, with an apparatus dealing with 300 cubic metres of air per hour, Claude was able recently to obtain with the greatest ease 90 cubic metres per hour of

\* Proceedings, November 16th, 1903.

nitrogen testing 99.6 per cent. What are the advantages of the system? They are most important. In the first place, if we wish to make concentrated oxygen, since we directly obtain a liquid holding all the oxygen of the air and testing 47 per cent. and no longer 21 per cent., as is the case with total liquefaction, we do away in the eventual evaporation with all that portion comprised between 21 and 47 per cent.

Now, it suffices for us to refer to the Linde's evaporation curves to be convinced that in this part of the evaporation *one third* of the oxygen is given off at compositions comprised between 7 and 21 per cent., and therefore inferior to the composition of atmospheric air, and hence useless. Doing away with this portion of evaporation by directly securing a highly oxygenated liquid is consequently to increase the yield of oxygen by 50 per cent.

On the other hand, we have seen that the gaseous residuum of liquefaction is constituted of nitrogen, to whose degree of purity limits cannot be assigned, as it chiefly depends on the dimensions of the bundle. Now, this pure nitrogen cannot be obtained directly by the processes founded upon total liquefaction, since the 21 per cent. liquid which they furnish, even at the commencement of evaporation, gives off 7 per cent. oxygen gases. This very simple preparation of pure nitrogen by the backward return is still one of the great advantages of this method, because it is very certain that the industrial realisation of this substance for the practical manufacture of ammonia, of the cyanides, of cyanamide, etc., must at no distant date be one of the most interesting features of the industry with which we are dealing.\*

Fig. 132 shows how Claude profited for the first time

\* We shall see further on the process for the production of pure nitrogen which Claude uses at the present time.

by these facts\* in an apparatus for the continuous manufacture of super-oxygenated air.

The compressed and cold air is delivered by two exchangers, M and N, in a contrary direction to the products of separation, and is passed through T in the inclined tubular system A, immersed in the liquid which is in the course of evaporation. The air condensed by the backward return is collected in C, and sent thence to overflow into V through a regulating valve R.

The gaseous residue, composed of nitrogen, escapes through S and is collected at the bottom of the exchanger M. The evaporated gases, composed of the super-oxygenated air, are collected after their passage through the exchanger N. This arrangement is now replaced by that shown in Fig. 130.

Although the author, as he has stated, intends to dedicate a separate work to the uses of oxygen and nitrogen, he cannot refrain from pointing out that by thus realising with unparalleled simplicity the continuous separation of the air into pure nitrogen and super-oxygenated air testing practically 40 per cent. of oxygen, an industrial problem of the highest importance has been solved, the pure nitrogen being utilised in the manufacture of cyanamide and the super-oxygenated air being able to be simultaneously used with great advantage in the same electrical works for the manufacture of nitric acid by being passed through special electrical furnaces.

It should be noted that in the description of the patent given above, insistence at great length has been made on the fact, of the circulation of the liquid to be evaporated being carried out in the reverse direction of the gases, the liquid which is best evaporated, and therefore the warmest, brings about the liquefaction of the more condensable portions, while the more refractory gaseous residue has at

\* French patent 324460, and certificate of addition 1089 of 1902.

its disposal, for liquefying it, the coldest liquid. Liquefaction can thus be achieved at the lowest possible pressure.

Considerations of this kind, which found themselves for the first time taken into account in this industry, present in practice a very great importance. We know, moreover, that it is the compression to be given to the air under treatment, which constitutes the essential factor of the cost in liquefaction. Now, this pressure depends to such an extent upon the composition of the liquids that it would be zero in 47 per cent. liquid air, while it attains 3·5 to 4 atmospheres in liquid oxygen.

We have also indicated, like Le Sueur and various other authorities, that the pressure of the gas to be liquefied is replaced by a suitable degree of vacuum maintained over the liquid to be evaporated.

## CHAPTER XVIII

### RECTIFICATION

Up to this point solely *super-oxygenated air* has been dealt with, which is the only result to which in practice the progressive evaporation of liquid air permits us to attain. We know with certainty, in what a disastrous manner the yield in oxygen culminates, as soon as we try to push its concentration a stage further, and how willy-nilly the obtaining of this super-oxygenated air was the only outcome, if it was not the only objective, of the early stages of this industry.

At the present time we have become more exacting. It is neither more nor less than *pure oxygen* which we demand—and which we know how to obtain—and we shall see with what marvellous ease, thanks to methods of *rectification* copied from those used in the alcohol industries, this has been effected.

The principle underlying this rectification consists in causing the oxygen vapours, derived from the evaporation of liquid air, to pass through the poor liquids obtained by means of the concomitant liquefaction, so as to condense the oxygen in these vapours in contact with the nitrogen instead of allowing them to be lost. The principle depends therefore upon constituents wholly similar to those which we have seen applied in the case of the *backward return*, and here again Baly's curves will be our sole guide.

It has been already stated that the first idea of the rectifying process appeared in a French patent obtained by

Claude in 1900 for the manufacture of oxygen; led, however, in a mistaken direction by the ideas prevalent at the time concerning the simultaneous condensation of oxygen and nitrogen, Claude laid down in this patent certain conditions as necessary which would be wholly unacceptable in practice.

On the other hand, the possibility of this rectification has been pointed out by Le Sueur in the same interesting patent,\* where, as we have already seen, the idea of the antecedent liquefaction of oxygen is advanced. We should remember also Thrupp's idea, already alluded to previously, of enriching the liquid air to be evaporated by causing cold atmospheric air to bubble through it, which, according to Baly's curves, should enrich it up to 48 per cent.

**Linde's apparatus** (1902).—From the practical point of view it is again to Professor Linde that the great honour is due of being the first to perfect the remarkable apparatus producing pure oxygen with ease and in large amounts by means of rectification.†

The following is a description of his process, which at the present time is used in a great number of installations producing from 2 to 20 cubic metres of oxygen per hour one of which, that belonging to Mr. Bardot, of Paris, produces as much as 50.

Here, unlike what takes place in all the preceding apparatus, and with the exception of the period of filling-up and of starting work, the liquid which is evaporated is continuously and exclusively *practically pure oxygen*. This liquid is placed in a receptacle *v* (Fig. 133), and its evaporation is set going by the *total* liquefaction of cold and compressed air which feeds the tubular body *r*.

The vaporised oxygen ascends the rectifying column *c*

\* Canadian patent No. 74430.

† French patent (307841), February 5th, 1901.

‡ German patent 173620, February 27th, 1902.

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FIG. 133.—Linde apparatus for pure oxygen.

emptying, this liquid attains a very low temperature because of its high percentage of nitrogen.

By virtue of its temperature, the liquid, during its descent, actively condenses the oxygen, in the ascending gases, which is added to the 21 per cent., already contained *ab initio* in the liquid at its entry in the column. This liquid, therefore, goes on progressively getting richer

Claude in 1900 for the manufacture of oxygen; led, however, in a mistaken direction by the ideas prevalent at the time concerning the simultaneous condensation of oxygen and nitrogen, Claude laid down in this patent certain conditions as necessary which would be wholly unacceptable in practice.

On the other hand, the possibility of this rectification has been pointed out by Le Sueur in the same interesting patent,\* where, as we have already seen, the idea of the antecedent liquefaction of oxygen is advanced. We should remember also Thrupp's idea, already alluded to previously,† of enriching the liquid air to be evaporated by causing cold atmospheric air to bubble through it, which, according to Baly's curves, should enrich it up to 48 per cent.

**Linde's apparatus** (1902).—From the practical point of view it is again to Professor Linde that the great honour is due of being the first to perfect the remarkable apparatus producing pure oxygen with ease and in large amounts by means of rectification.‡

The following is a description of his process, which at the present time is used in a great number of installations producing from 2 to 20 cubic metres of oxygen per hour, one of which, that belonging to Mr. Bardot, of Paris, produces as much as 50.

Here, unlike what takes place in all the preceding apparatus, and with the exception of the period of filling-up and of starting work, the liquid which is evaporated is continuously and exclusively *practically pure oxygen*. This liquid is placed in a receptacle *v* (Fig. 133), and its evaporation is set going by the *total* liquefaction of cold and compressed air which feeds the tubular body *r*.

The vapourised oxygen ascends the rectifying column *c*,

\* Canadian patent No. 74430.

† French patent (307841), February 5th, 1901.

‡ German patent 173620, February 27th, 1902.



which is at the top of the apparatus, in a contrary direction to, and in contact with, liquid air testing 21 per cent. formed in F, which is, by means of its pressure, emptied continually at the top of the column C. At the instant of

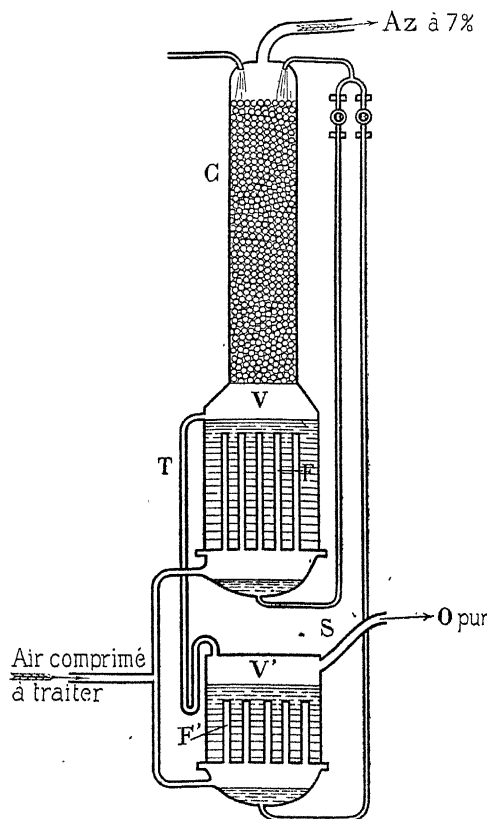


FIG. 133.—Linde apparatus for pure oxygen.

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in oxygen, and in this way reaches the evaporator in the condition of *pure liquid oxygen*, which replaces continuously the oxygen which is evaporated therein.

It is possible that at first sight the rationale of the system may not be very apparent to the reader. What is the use, he will say, of evaporating continuously the liquid oxygen in *v* to replace it therein not less continuously by means of the descending liquid?

Here is the reason:

We have just now observed that the condensed oxygen unites in the descending liquid with the 21 per cent. which exists therein already; at each instant, therefore, the evaporator receives a *little more* oxygen in a liquid condition than issues from it in a gaseous condition. A portion of the liquid may therefore be continually passed over through the overflow pipe *r* into a second evaporator *v'* similar to the first, and the evaporated oxygen in this second evaporator, by means of the compressed air in *r'*, is expelled through *s* across a temperature exchanger to the gas-holder or the apparatus where it is utilised. It is then the final product of manufacture, and this product is indeed, as we have seen, as nearly as possible pure oxygen. It tests in practice 96 to 98 per cent. The liquid air which is reconstituted in *r'* is naturally united to that formed in *r*, and sent therewith to the top of the column *c*.

To estimate the yield of this process let us follow up the ascending gases—which are progressively despoiled of oxygen by the increasingly cold liquids which they meet, and issue at the summit of the apparatus impoverished down to the theoretical 7 per cent., which, in accordance with Baly's curve, corresponds to the extreme point of separation for a 21 per cent. liquid.

Now if four fifths of the air escapes with 7 per cent. of oxygen, equivalent to the theoretical loss of a little under one third of the oxygen present in the air treated, that

evidently means that we have extracted, in the form of pure oxygen, the other two thirds. The result is satisfactory, and we cannot help admiring the extreme simplicity with which it is attained.

**Apparatus of Levy and Helbronner (1902), Pictet (1903).**—A very analogous process has been patented by Levy and Helbronner.\* M. Pictet has also patented in 1903 an apparatus designed to furnish pure oxygen by the process of rectification and which reproduced without any sensible alteration the essential characteristics of the Linde apparatus.

**Claude's apparatus.**—Notwithstanding its attractive appearance and its efficiency the Linde apparatus presents nevertheless a serious drawback. It only permits of the recovery of two thirds of the oxygen, and the other third is not only lost, but contaminates the nitrogen and deprives it of all value. This is, indeed, the common defect inherent in all systems based upon the *total* liquefaction of the air, since the liquid testing 21 per cent. which they yield in accordance with the curves can only deprive the gases of oxygen down to the limit of 7 per cent.

Claude has been able to avoid this serious defect in a very simple manner by combining with the process of rectification his device for the "backward return." It is the apparatus arranged on these lines which is working in all the installations erected in accordance with his methods, and there is good reason for believing that with the exception of the exclusive evaporation of pure oxygen, the processes of the future will not essentially depart therefrom.

The liquid to be evaporated is still pure oxygen, but there is only one evaporator, which furnishes at one and the same time the one fifth of the oxygen, constituting the manufactured product, and the four fifths destined to carry out the rectification.

\* English patent No. 16615, of July 26th, 1902.

The air to be treated, which is initially cooled in the exchangers, arrives at the bottom of the tubular receptacle, F, immersed in liquid oxygen. In rising through F it is

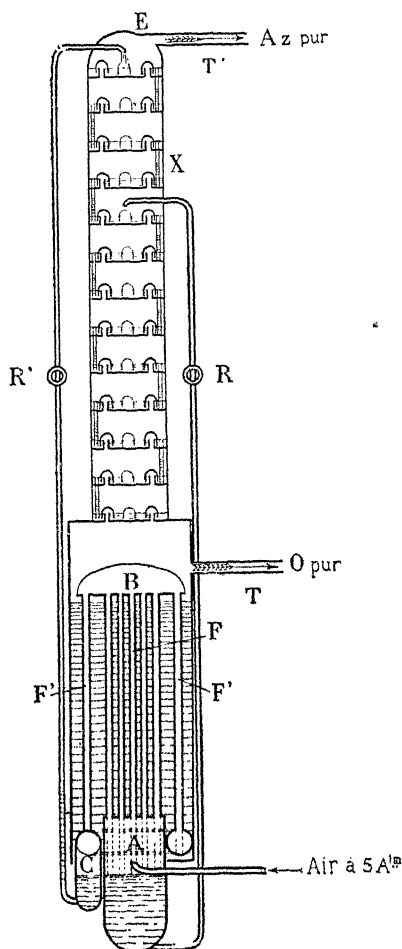


FIG. 134.—G. Claude's apparatus for the separation of the air into pure oxygen and nitrogen.

partially liquefied, yielding a liquid, collected in c, containing the whole of the oxygen, and testing, as has been explained above, up to 47 per cent. oxygen, together with a gaseous residuum which is nearly pure nitrogen. The

latter, passing from above downwards through the tubular receptacle  $F'$ , which is concentric to the first receptacle, completes its liquefaction, yielding therefore, liquid nitrogen, which is collected at  $c'$ .

The rich liquid formed in the central receptacle is caused by reason of its pressure to overflow in a continuous way into the central portion of the rectifying column; it exhausts the ascending gases, in accordance with the curve, down to about 21 per cent. The liquid nitrogen passes over at the summit of the column, and subjects the 21 per cent. gases derived from the preliminary rectification, because of its  $3^{\circ}$  to  $4^{\circ}$  C. lower temperature, to a supplementary rectification which, according to Baly's curves, deprives them entirely of oxygen. It is, therefore, practically pure nitrogen which escapes at the top.

Resuming, the entire amount of nitrogen is delivered from the top of the apparatus, the entire amount of the oxygen is delivered at the level of the evaporator.

In this fashion the entire separation of atmospheric air into practically pure oxygen and nitrogen is realised by means whose simplicity is obvious.

This apparatus is used in all installations for the production of pure oxygen constructed by the "*Société l'Air liquide*" (the Liquid Air Co.).

The liquid air added is here assumed to be derived from a special liquid air machine.

It will be seen presently, however, that Georges Claude has succeeded in combining in a practical manner—and this he employs by preference—the other method of compensating for the losses in cold to which allusion has been many times made in the preceding pages. The air to be treated is compressed more than is necessary to liquefy it in the tubular holder, and is brought to the required pressure in a machine where it is expanded, this machine, which is capable of furnishing exactly the compensation

necessary for the losses in cold, having been added in series. Thus, the whole of the air used is separated into its elements, and the simplicity of the apparatus attains a maximum in the system known as the "*single cycle*," as distinguished from the system of the "*double cycle*," where a portion of the air under high pressure is only utilised for the production of the added liquid air, and is lost as far as the oxygen is concerned.

An objection which has often been advanced as of most serious import should here be refuted.

Both one and the other of the two tubular holders in the apparatus (Fig. 134) are immersed in liquid oxygen; they are consequently submitted over their whole surface to a temperature which is sensibly uniform. How, under these conditions, can it be contended that it is possible to obtain separately as liquids 47 per cent. oxygen on one side and nitrogen on the other, whose temperatures of formation, according to the data given in Baly's tables, actually differ by  $4^{\circ}\text{C}$ .? It would seem, *à priori*, as a matter of fact, that if the temperature of the liquid oxygen bath is suitable for the condensation, under the pressure employed, of the 47 per cent. liquid in question, it must be too high by  $4^{\circ}\text{C}$ . to condense the nitrogen.

Wherefore, either the apparatus above described is faulty, and the two liquids collected in the two tubular receptacles are identical, or the nitrogen is not condensed and the second receptacle is practically useless.

In spite of its scientific character the objection is not very serious. To admit that the temperature in the interior of the tubular receptacles is unavoidably equal to that of the external liquid oxygen is just as reasonable as to admit that when an electric accumulator is charged, its electro-motive force is unavoidably equal to the difference of potential applied at its terminals. For it is admitted that if this were the case, the accumulator could never be

charged; while, if it be desired that the contrary should be the case, it is necessary to increase the difference of potential acting on the terminals above the electro-motive force; the more this difference is increased the more the intensity of the charging current is increased, the excess in difference of potential over the electro-motive force being indispensable to compensate for the loss of potential due to the delivery itself. The case we have been considering offers an exact parallel to this. If the pressure in the tubular holder is just low enough to permit a trace of 47 per cent. liquid to appear, the temperature is effectively uniform and exactly equal throughout the whole interior of the holder to the temperature of the external liquid oxygen.

If it be desired to liquefy in a practical manner it is necessary to increase the pressure; this being effected, the temperature of the 47 per cent. liquid is necessarily raised above that of the external liquid oxygen; practical liquefaction therefore calls for a transmission of the heat of the gas which is being condensed in the direction of liquid oxygen, and just as an electric current entails a fall of potential proportionate thereto, the heat-current here produced brings about a fall of temperature in the conductor traversed, that is, from one wall to the other of the tubes of the holder. From thence onward, the temperature in the interior of the tubes of the holder, instead of being everywhere equal to that of liquid oxygen, exceeds it wherever there is liquefaction, and to an increasing extent the more abundant the liquefaction is at the point in question; at the bottom of the holder the internal temperature is notably higher because of the abundant generation of 47 % liquid, which is readily condensable; proportionately as we rise in the holder and the gaseous residue is less condensable, the temperature decreases progressively down to the point where condensation becomes *nil*, and where as a

consequence the internal temperature is that of liquid oxygen. Above this level naturally there is no liquefaction. The level of this point and the energy of condensation can be raised by again increasing the pressure, and a point will be reached where the pressure applied will be such that the temperature of subsistence of the liquid nitrogen itself will be raised above that of the exterior liquid oxygen, and consequently where liquefaction can be effected abundantly, even when the nitrogen of the second holder is concerned.

This train of reasoning, though somewhat lengthy and subtle, possesses the undoubted advantage of definitely clearing up the progressive increase in test which is essentially characteristic of the descent of liquids in the reversing process. It is manifest, in point of fact, that these liquids not only meet, in the course of their descent, gases which are more and more rich in oxygen, but also temperatures which are less and less low, consequently less and less favourable to the existence of nitrogen in the liquid form. It is also evident, as a consequence of the preceding, that it will be possible to change at will the ratio of the liquefaction in the two tubular holders by simply changing the pressure of liquefaction, and consequently the output; the higher the pressure, the more will be liquefied on the nitrogen side, consequently the more the liquid in the first receptacle will approach the limiting test of 47 per cent., but at the same time the more will the nitrogen tend to become impure. It is evident that an exact proportion between the two receptacles will have to be established, taking into account these facts and the magnitude of the output, and also taking into consideration the fact that the pressure of liquefaction should be as low as possible having regard to the expenditure of motive power, and having regard also to the evaporation which occurs at the instant of overflow of the laxivating liquids in the rectifying column, and which adds most unfortunately to their content



of oxygen. The pressure in question is, in the Claude apparatus, generally comprised between three and four atmospheres.

The above consideration of the various relative tests which it is possible to obtain in the two liquids thus produced, through a simple variation in pressure, leads us to ask ourselves what are the conditions the two liquids must obey to attain exact rectification. We have admitted up to this point that, subject to the condition of pouring in pure liquid nitrogen at the top of the rectifying column, the gaseous nitrogen is also given off in a state of purity. Now this would be tantamount to getting over the difficulty too cheaply. The condition above enunciated is necessary, but not sufficient. Another condition, not less necessary and as self-evident, is that the *quantity* of the liquid nitrogen shall be sufficient—sufficient to retain the whole of the oxygen which has escaped the first laxivating liquid; otherwise the law of concomitant tests will not have been fulfilled at the top of the column.

Now, supposing that the separation thus obtained by the reversing process is accomplished with theoretical exactitude, and produces as liquids pure nitrogen and 47 per cent. oxygen.

The 21 per cent. oxygen in 100 parts of air treated will yield—

$$x = \frac{21}{0.47},$$

or 45 parts of the 47 per cent. liquid, while the pure nitrogen will form 55 parts. The available capacity for absorption of these 55 parts is evidently limited by the quantity of oxygen which must replace the nitrogen therein, to bring up its test to that of the first laxivating liquid, viz. 47 per cent.

The capacity for absorption is therefore—

$$55 \times 0.47 = 26 \text{ parts of oxygen.}$$

Now the 79 parts of gas which will issue at the top of the apparatus in the condition of nitrogen, pass the level where the enriched liquid is added, exhausted down to 21 per cent. by the united volumes of the two laxivating liquids. They consequently contain—

$$79 \times 0.21 = 17 \text{ parts only of oxygen.}$$

The quantity of liquid nitrogen is therefore not only sufficient, but, in fact, super-abundant, to ensure a complete separation, and there is a very large margin to provide for unavoidable imperfections.

#### THERMO-DYNAMIC YIELD OF THE SEPARATION OF THE ELEMENTS IN THE AIR BY WAY OF LIQUEFACTION.\*

We have demonstrated in what has preceded (p. 292) the theoretical necessity for an expenditure of energy to effect the separation of gaseous mixtures.

It will not be uninteresting to examine how this necessity has to be interpreted for air in the process of separation *by liquefaction*, and what is the discrepancy between theory and the results obtained experimentally, and what the discrepancy between theory and the results obtained in practice by means of the process which has been described above.

If we consider, in the first place, a simple fluid, it is apparent that 1 kg. of this fluid, taken in the liquid state, demands for its evaporation, and then for its heating up to the surrounding temperature, a quantity of heat exactly equal to, and of precisely the same quality as, that set at liberty by cooling, followed by the liquefaction of 1 kg. of the same fluid taken at the ordinary temperature and under the same pressure. If the temperature exchangers are perfect, the difference of pressure permitting the evaporation and the accompanying liquefaction is infinitely small; the fluid in question is able to pass

through the complete cycle of cooling, liquefaction, evaporation and heating, and return theoretically to its initial condition without expenditure of energy.

But in the case of air, it is no longer necessarily the same, because the air being a mixed fluid, neither its temperature of condensation nor its temperature of evaporation remain constant.

Thus the atmospheric air commences to liquefy without pressure, and even under a pressure less than 1 atmosphere, into liquid air testing 21 per cent., because it condenses initially from 47 per cent., which is less volatile than the 21 per cent. But we know that in proportion as we have to deal with a richer liquid its temperature becomes higher, and the evaporation and accompanying liquefaction can no longer be obtained, save by the progressively greater compression of the air to be treated. If, in particular, the object sought is the complete separation of the oxygen and nitrogen, the obvious necessity of thereupon evaporating pure oxygen, wholly or partially, whose point of ebullition exceeds by some 12 per cent. that of liquid air, necessitates the compression to the extent of from 3 to 4 atmospheres of the whole or a part of the air to be treated.

The cycle, in this case, cannot any longer therefore be followed without expenditure of energy, so that the difference in the boiling-points of the elements to be separated, which is the measure of the separation, appears to be at the same time the origin itself of the expenditure of energy foreseen theoretically. A rather curious anomaly should, however, be noted. According to the theory in question (p. 292), the theoretical work of separation of a gaseous mixture is equal to the sum of the individual work of compression of each of the constituents from its partial pressure up to its total pressure. Such work is evidently independent of the nature of the constituents, since the work

of compression for equal volumes is the same for all gases, which are condensable with difficulty. On the contrary, in the process of separation by the method of liquefaction, the pressures which have to be applied, and hence the work required to perform the cycle, depend essentially upon the difference between the elements to be separated from the standpoint of liquefaction. If, therefore, this difference is small, it may happen that the cycle is carried out with a very small expenditure of energy, inferior to that required theoretically.

Now this abnormality is only apparent.

It simply tells us that, in this case, the process in question is incapable of realising an incomplete separation, which is not astonishing, because the concomitant gaseous and liquid phases are here in all cases sensibly identical. Let us insist further on this point.

We have neglected up till now the consideration of the special method of working employed for the separation.

In point of fact, a rational process consists in employing the Claude arrangement for the retrograde process, which offers, in point of fact, the scope of a general method. Thanks to this arrangement, it is possible to separate the mixture into a liquid, *a*, comprising the whole of the less volatile element in the liquid state with the test which can co-exist with the constitution of the said gaseous mixture—that is 47 per cent. in the case of atmospheric air testing 21 per cent.—and into a liquid *b* comprising the more volatile element alone. With these two liquids, the products of the concomitant evaporation in a suitable rectification column are successively rectified. Liquid *a* rectifies them up to the test corresponding to its own, that is, from 21 per cent. in the case of our liquid, to 47 per cent., in such a way, and this is a fact of general application, up to the level of admission of liquid “*a*,” the rectified gases existing theoretically at the very composition of the mixture treated. Liquid *b*

completely exhausts them. Now, the greater the difference of the volatility of the elements, and therefore the greater the pressure required to complete the cycle, the higher the test of *a*; thus, oxygen and nitrogen being supposed to be more dissimilar, liquid *a* in correspondence with the air might test, for example, 60 per cent. instead of 47 per cent., consequently the more abundant liquid *b* would become, and the higher its rectifying value would be, since this is measured by the difference in the tests of *a* and *b*.

If, therefore, the difference between the respective volatilities is small, there will be little of liquid *b* generated, and it will be of small efficiency: the second liquid will be able to retain very little of the less volatile element, which escapes from the first liquid, as we have said, with the very test of the gaseous mixture employed. Thus, the operation costs little, but, as it has been shown, the separation is incomplete, and yields only a little of the less volatile element.

If the difference between the volatilities is, on the contrary, very great, great pressure is required; liquid *l* is at the same time both very abundant and very efficient, there is too much of it for the requirements of the operation; the separation is complete, but it costs too much energy.

Now, in the case of air, we have seen that the second liquid (nitrogen) is produced in such an amount that it is just able, with a reasonable theoretical excess, which is useful to avoid being troubled with the practical imperfections of the operations, to absorb from the first the whole of the oxygen escaping. The separation can therefore be complete, while calling for almost a minimum expenditure of energy, so that the process in question can be applied to the separation of the air under conditions which are particularly advantageous. It was interesting to draw attention to this fact.

It is doubtless due to this advantageous circumstance that the apparatus which we have been considering possess their high output. This output, in apparatus producing 50 cubic metres per hour on the system above described, amounts to 1 cubic metre of pure oxygen per effective horse-power hour on the compressor shaft. The results already

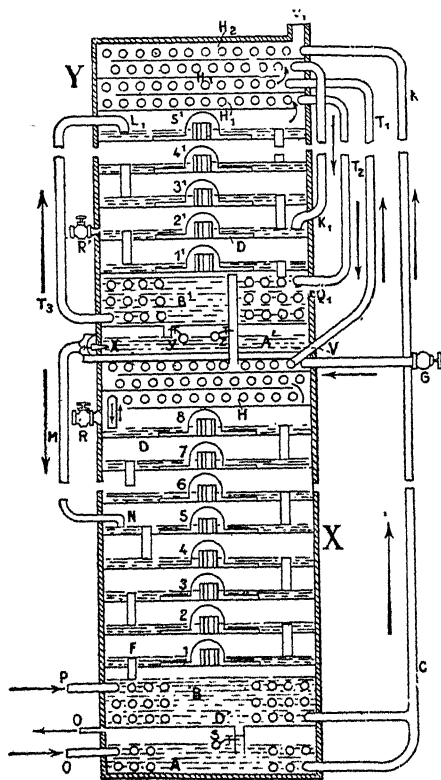


FIG. 135.—Levy and Helbronner's apparatus for liquefaction.

obtained certainly warrant us to consider as assured the obtaining of  $1\frac{1}{2}$  cubic metres per horse-power hour with larger apparatus. If we take into consideration the very low efficiency of the present compressors, viz. about two thirds, and the theoretical figure of 9 cubic metres per horse-power hour laid down previously (p. 295), this points to 25 per cent. as the proper thermo-dynamic efficiency

possible with this method, and even higher if we consider the possibility of effecting a portion of the liquefaction of the air treated in colder liquids than oxygen.

**Re-liquefaction (Levy and Helbronner).**—We have seen the importance of the progress which the Claude apparatus owes to the delivery of the liquid nitrogen as a laxiviator at the top of the rectifying apparatus. Now, the principle of this process has been conceived independently of Claude and realised by entirely different means ever since 1902,\* by Messrs. Levy and Helbronner, whose patents have been secured subsequently by the *Société l'air liquide*.

The process of these inventors, who liquefy their air in the same way as Linde, in one sole mass testing 21 per cent. oxygen, consists, as in the case of Linde, in bringing about with this liquid a rectification of the gases evaporated in a column x, whence issue, as a consequence, through r gases testing 7 per cent. of oxygen; but instead of working at the atmospheric pressure, the operation, owing to the employment of a sufficient initial pressure, is itself carried out under pressure. Because of this pressure these 7 per cent. gases become reliquefied in a system of tubes which crowns the rectifying column, immersed in a liquid bath b boiling at atmospheric pressure. This bath is fed by the reliquefied liquid, which is delivered at the top of a second column v, and descends in the opposite direction to the products of evaporation. These products are naturally washed by the laxivating liquid, testing 7 per cent. down to a very low test of about 2 per cent., according to Baly's curves, and consequently almost pure nitrogen is given out at v, whose test might still be considerably lowered, by means of a renewed increase of pressure as suggested by the inventors, in a third liquefaction in a third column.

\* German patent 158838 of November, 1902.

## MANUFACTURE OF PURE NITROGEN.

**Production of pure nitrogen—Levy's process.**—We have now reached a whole class of apparatus characterised by what is styled the *auto-progressive* purification of the nitrogen, whose employment has acquired a considerable importance, because of the necessity for obtaining an extremely pure nitrogen, with a minimum of 99·5 per cent. in the manufacture, already largely developed, of *cyanamide* or lime nitrogen. We have observed above (p. 369) that this degree of purity is not by any means above the capacity of the very simple method of the retrograde process.

However this may be, these are the essential features of the principle of the auto-progressive rectification of the nitrogen, conceived at an interval of only a few days in France by R. Levy,\* and in Germany by Professor Linde,† who also equally intervene in the retrograde process as we have had the occasion to point out.

We will start by indicating, with slight modifications, the form realised by Claude's lamented collaborator, Levy, who has just met his terrible fate in the catastrophe of the "Titanic" when going back to his appointment in the Claude Works at Montreal.

The air to be treated is entirely liquefied in the tubular system s, while bringing about the evaporation of the external liquid, of which one fifth is withdrawn through m and through an exchanger for delivery to the apparatus, where it is utilised; the other four fifths rise in the rectification column x, and there are subjected to a rectification, at the expense of the 21 per cent. liquid entering at 8, which, owing to an initial high pressure, can be carried out *under pressure*.

The 7 per cent. nitrogen, which results from this

\* French patent March 1898



rectification, is taken off much below the point 8, where the 21 per cent. liquid is introduced into the rectifying column, and sent into an apparatus, either a piston machine or turbine, where it is expanded down to atmospheric pressure. The liquid, very rich in nitrogen, produced by this expansion is poured out on to the plates 10 and 9

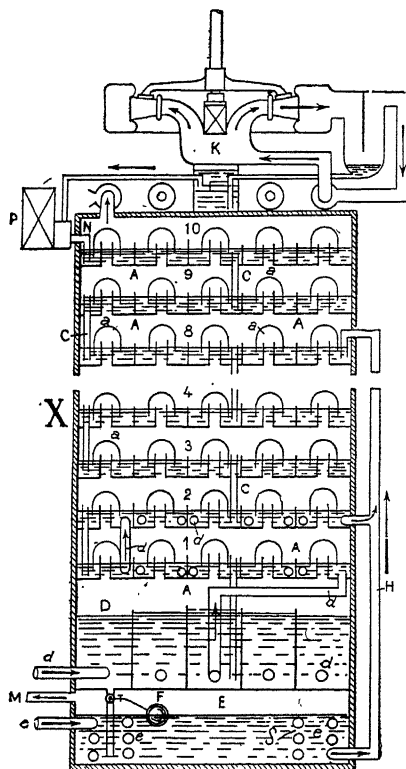


FIG. 136.—Apparatus for pure nitrogen—Levy's system.

and, as in the Claude process, acts as a laxiviator to diminish the proportion of oxygen in the ascending gases. Now it is at this stage that the interesting idea of the auto-progression of the rectification comes into play; immediately the supplementary laxiviation is initiated the nitrogen reaches the top in a slightly purer state. It,

*slightly less oxygenated*, which will exhaust the ascending gases slightly more, and so on; so that, if the quantity of liquid formed at  $\kappa$  be sufficient, the tendency towards a stable equilibrium will be automatic and energetic, which will correspond to the formation of an absolutely pure nitrogen. It is abundantly evident that to attain this result it is necessary that the valve where the oxygen issues at  $m$  must be sufficiently open to admit of the whole of the oxygen escaping; to be perfectly assured on this point, it is even desirable to allow a notable quantity of nitrogen to escape with the oxygen, so that if the desired result is essentially to obtain absolutely pure oxygen, it will be rather difficult to obtain at the same time the oxygen in a state of great purity; its test will probably hardly exceed 90 per cent. These remarks, however, are applicable to all systems; to collect one of the two gases in a very high degree of purity, it is necessary to collect a little less in amount, and allow the remainder to escape with the other element to be assured that the reverse is not produced.

**Production of pure Nitrogen: Linde's process.**—The auto-purifying process of Linde (Fig. 137) is precisely the same as that of Levy, with the exception of the method of obtaining the liquid nitrogen. In accordance with the ordinary arrangement of the Linde apparatus, the evaporator  $e$ , placed at the bottom of the column  $g$ , only furnishes the oxygen necessary for the rectification, which is effected without pressure down to 7 per cent. in this column  $g$ . A portion of the liquid of  $e$  is raised in the worm  $l$ , which performs the function of evaporator for that portion of the oxygen which is destined to be collected; so this liquid oxygen is given the capacity of liquefying the gaseous nitrogen in which the worm is immersed, through making it boil under a reduced pressure, produced by a

exactly, the nitrogen tending, more and more, to the condition of purity to which it would attain, provided the quantity of laxivating liquid produced in contact with  $i$  be sufficient. Now, under the circumstances, a calculation, similar to that on p. 383, shows that this would not be

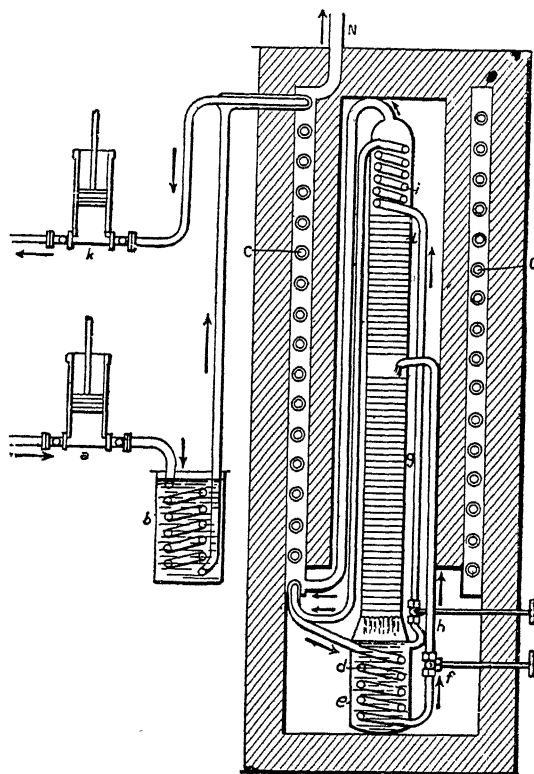


FIG. 137.—Apparatus for pure nitrogen—Linde's first form.

the case if the liquid ascending in  $i$  represented, strictly, one fifth of the air treated, and corresponded, therefore, to the conditions for obtaining pure oxygen. It is therefore impossible to obtain by this method a total separation, and we shall not reach the point of obtaining sufficient laxivating liquid accompanied with a quantity of nitrogen almost equal to its own proper amount, so that the result of the

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manufacture will be then pure nitrogen, and at most some 60 per cent. oxygen.

In another process (Fig. 138), to which in practice, in spite of its complexity, Dr. Linde gives the preference, this inconvenience is avoided. He recovers a part of the

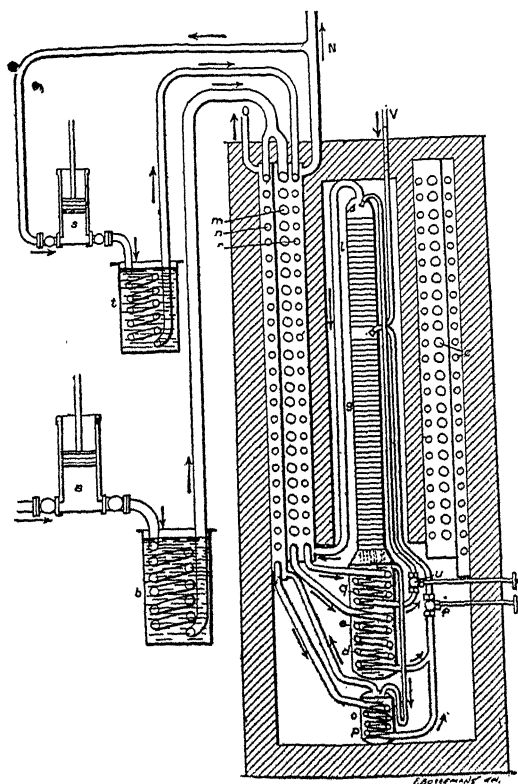


FIG. 138.—Apparatus for pure nitrogen—Linde's second form.

nitrogen which escapes from the apparatus at the ordinary temperature after it has passed into the exchangers; he compresses it under a pressure of some atmospheres and sends it through an exchanger to be liquefied by means of its pressure, and through a second submerged tubular system *q*, similar to that where the air to be treated is liquefied, into the liquid oxygen to be evaporated. H

obtains in this way from the first a liquid testing 7 per cent. which he sends to empty itself, as in the Claude process, at the top of a prolongation of the rectifying column *g*; this liquid submits the ascending gases to a rectification which naturally lowers their test in oxygen, so that the liquid which is subsequently formed with the nitrogen will be a little poorer than the preceding liquid, will impoverish still further the rectified gases, and therefore by a sequence of identical effects the nitrogen will automatically reach a high degree of purity. Here, evidently, there are no limits to the quantity of laxivating liquid that it is possible to obtain.

It is this type of apparatus which is employed in the installations of the Sister Companies of the *Società Italiana per i Prodotti Azotati*, and it furnishes practically nitrogen free of oxygen, and only containing some traces of argon.

**New Linde apparatus.**—Finally, in a very recent process patented in 1907, Linde has sought to take advantage of the laxivation with liquid nitrogen, without the complicated and costly method to which recourse must be had in the apparatus previously described, and by harking back to the conditions of extreme simplicity by which Claude himself obtains this liquid nitrogen. He has described in this patent an arrangement which permits, as in the Claude

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that the ascending gas reaches the top *c* in the condition of pure nitrogen, which is partially liquefied in *s*, and serves to condense the ascending oxygen in the form of 47 per cent. liquid, and, as to the remainder, is liquefied com-

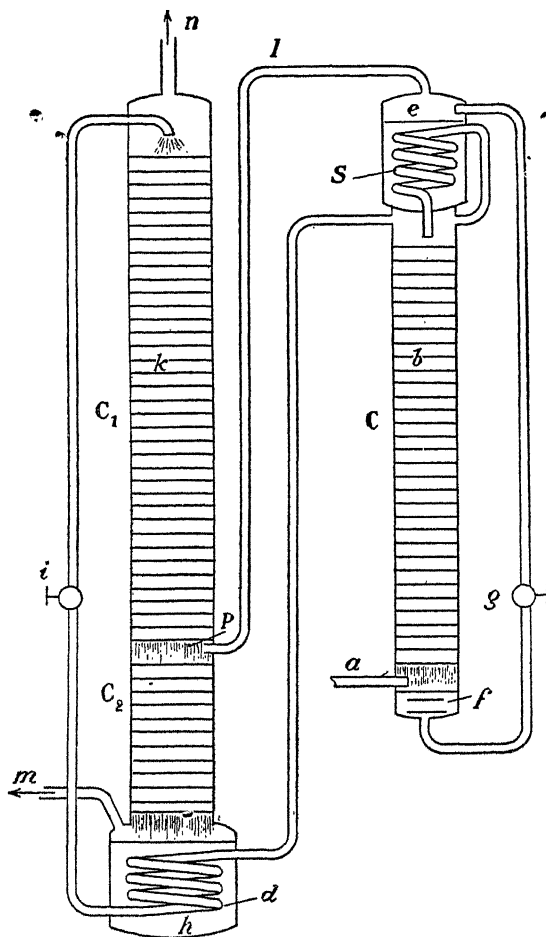


FIG. 139.—New Linde apparatus for obtaining pure oxygen and nitrogen.

pletely in the oxygen, and furnishes the liquid nitrogen, which is to be supplied at the top of the second column. It is the 47 per cent. liquid thus produced which emptied into *e*, initiated the first liquefaction, and the resulting gases of this evaporation and is supplied to the column at

the point  $p$  corresponding with their test. It will be seen that the modification introduced by Linde in the Claude method of working, for obtaining the two liquids identical to those produced by that method, consists primarily in pushing back the condensation of the air towards the top of the tubes composing the central receptacle (Fig. 134), and in depending solely on rectification for transferring to the liquid thus formed, the whole of the oxygen in the ascending air.

Better than any other, this latest process shows how close the inter-dependence of the principles involved in the Claude processes, those of Linde, and also those of Messrs. Levy and Helbronner, have become.

**Production of pure nitrogen by the G. Claude process.**—The success achieved by Linde in the direction of producing pure nitrogen, and the importance which this question has acquired by reason of the very rapid development of the cyanamide industry, induced Claude in his turn to tackle this question. In his case, moreover, the problem appeared to be considerably more simple. We have seen in fact, with what ease the backward return furnishes the liquid nitrogen necessary for the rectification of the evaporated gases; in principle this process achieves the complete separation of the air into pure oxygen and pure nitrogen, and we have not failed to bring this fact to the notice of our readers in the preceding pages. In practice, on the contrary, the laxivating liquid still contains from 4 to 5 per cent. of oxygen, and this is furthermore in too small a proportion to obtain the desired effect, because the residual nitrogen can only be condensed with considerable difficulty in the liquid oxygen of the vaporiser; thus with these apparatus we can only produce, under ordinary circumstances, nitrogen from 2 to 3 per cent. pure, and all the more so if it be desired to produce pure oxygen also. After numerous trials, Claude succeeded in arranging so

that the test of the residual nitrogen at the top of the tubes of the bundle for the backward return, when about half and half liquefaction is attained, should not be less than 99.6 per cent., showing how perfect is the exactitude of the phenomena of progressive condensation and of rectification which take place. On the other hand, the liquefaction of this residual nitrogen is facilitated by its no

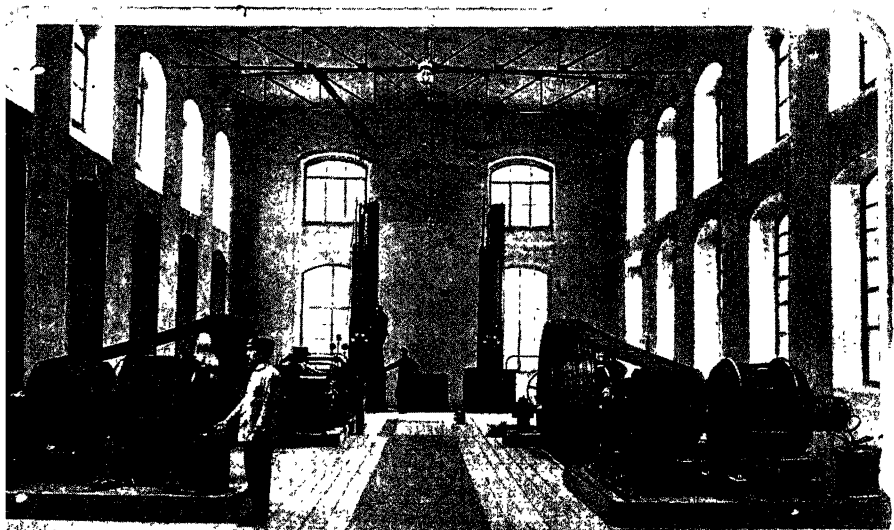


FIG. 140.—Interior of the Claude building at the Terni works.

longer being produced in the oxygen bath, but in liquids which are a little colder than this, viz. those which circulate at the bottom of the rectification column. In this fashion, and in all the requisite abundance, a laxivating liquid has been obtained which only tests from 0.3 to 0.4 per cent. of oxygen, and is capable of rectifying the 97 per cent. N, up to 99.9 per cent. The results obtained by this very simple process have been excellent, the oxygen being given



off on one side testing 80 per cent., and the nitrogen on the other containing not more than 0.2 per cent. of oxygen.

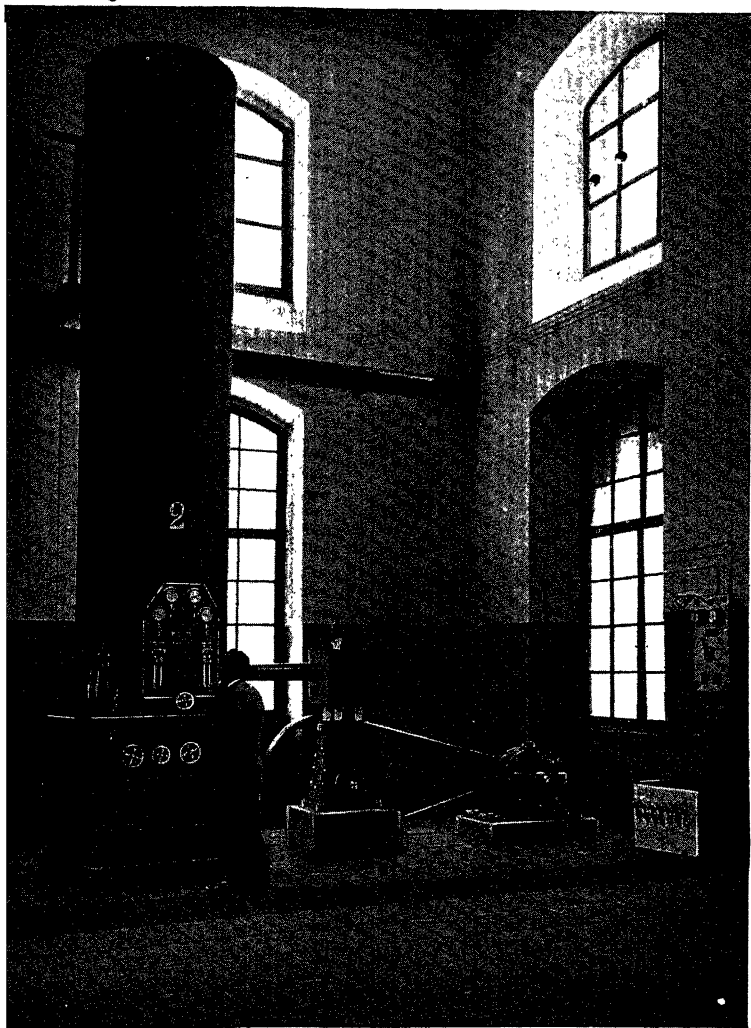


FIG. 141.—One of the two columns at the Terni works.

Two apparatus, the first constructed of this type, have been installed at the present time in the works of the Italian Company for Carbide of Calcium at Terni. They each of

them produce with the expenditure of 125 H.P. 400 cubic metres of nitrogen testing 99.7 per cent. per hour. Other two apparatus of 500 cubic metres and 98.9 per cent. purity are similarly working at Alby in Sweden; others also are in the course of erection or manufacture for Sweden, for Austria and for Switzerland.

It will be seen by these examples to what an ~~extent~~ this magnificent problem of the fixation of nitrogen has opened to the industry of low temperatures the period of important applications.

## CHAPTER XIX

### GROUPING OF THE APPARATUS

#### EXISTING INSTALLATIONS.

**Linde installations.**—There remains, to complete our task, to indicate the way in which the different component parts whose necessity we have demonstrated have been combined for practical purposes.

Fig. 142 represents diagrammatically a complete Linde oxygen installation.

Fig. 143 represents the appearance of such an installation in the case of a unit with an output capacity of 20 cubic metres of pure oxygen per hour.

The working is apparent by simple inspection of the diagrams; we will therefore elaborate certain particulars only.

The decarbonising of the air is effected before its compression by means of milk of lime flowing continuously in a contrary direction to that of the air. Drying, on the contrary, must be effected after compression, as the compressor comprises a jet of water which tends to render the compression isothermic.

This desiccation is effected by means of solid chloride of lime, which starts it, and of potash in lumps, which completes it.

The unit includes, in reality, two separating appliances,  $K$  and  $K'$ , so as to provide for uninterrupted working. It happens, however, as the desiccation

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complete, that the exchangers get choked up little by little; at the end of a certain time, which may attain eight days, the apparatus must therefore be stopped and the exchangers

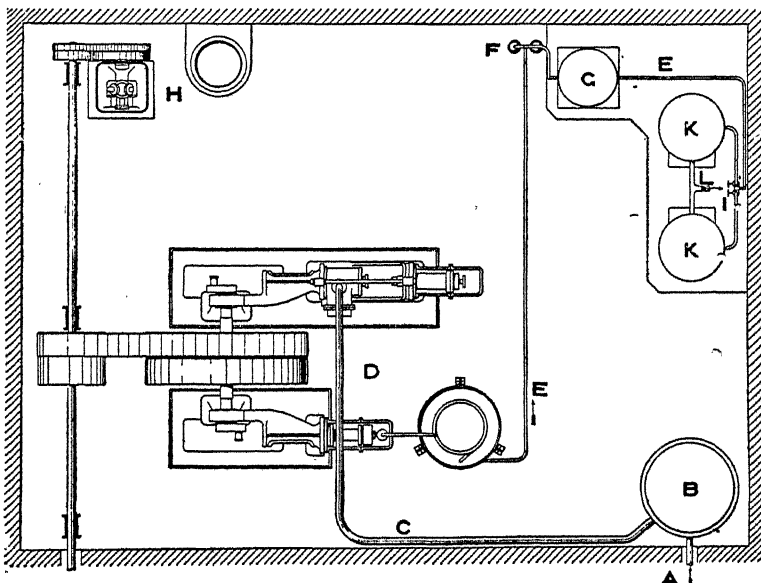
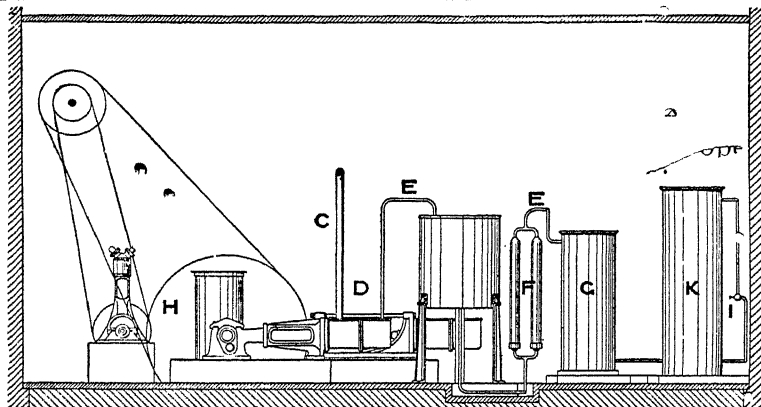


FIG. 142.—Diagram of an installation for pure oxygen on the Linde system.

thawed by heating up and energetic evacuation, at ordinary temperatures.

This is, moreover, a common characteristic both c

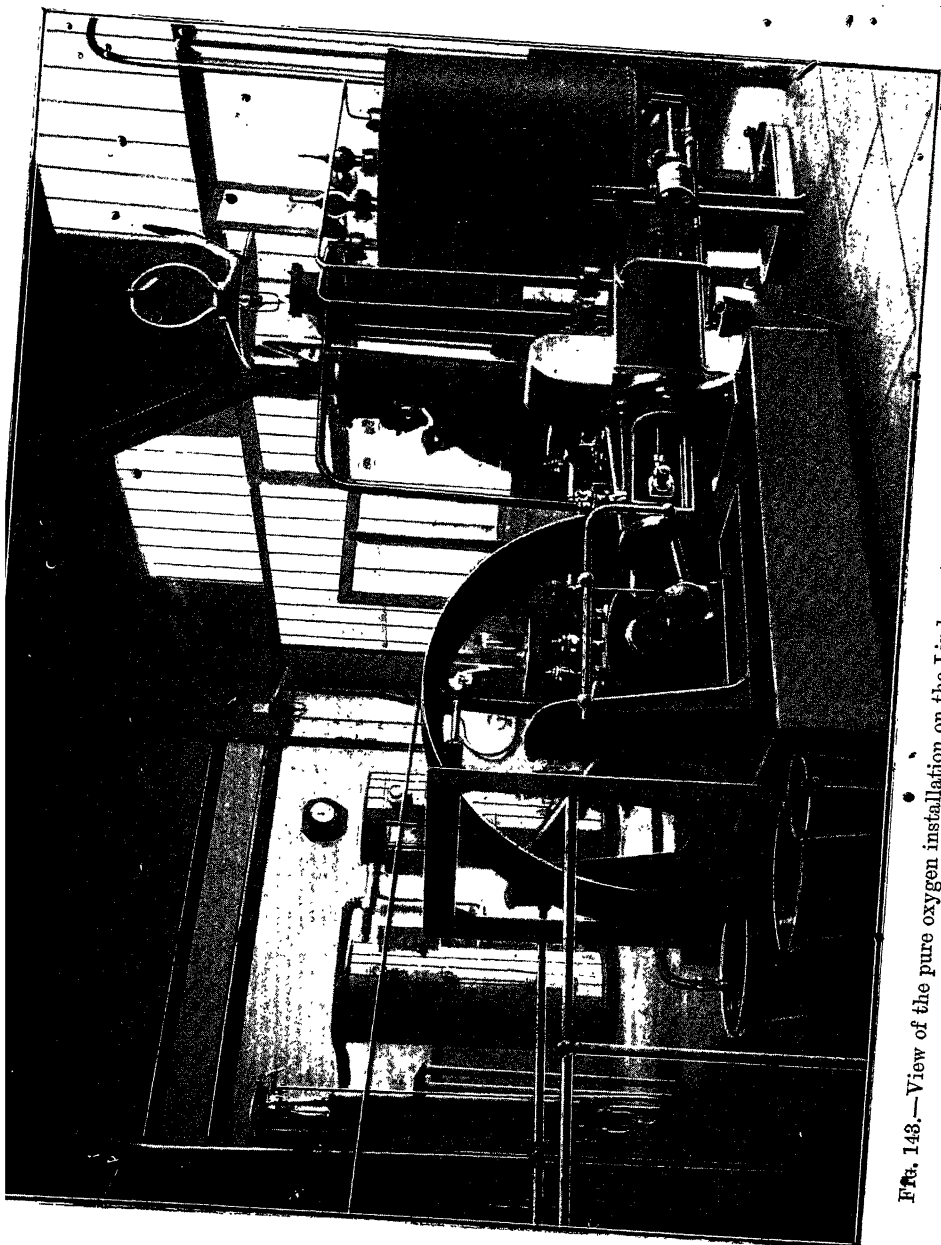


FIG. 143.—View of the pure oxygen installation on the Linde system belonging to M. Bardot, of Paris. Capacity of production 20 cubic metres per hour.

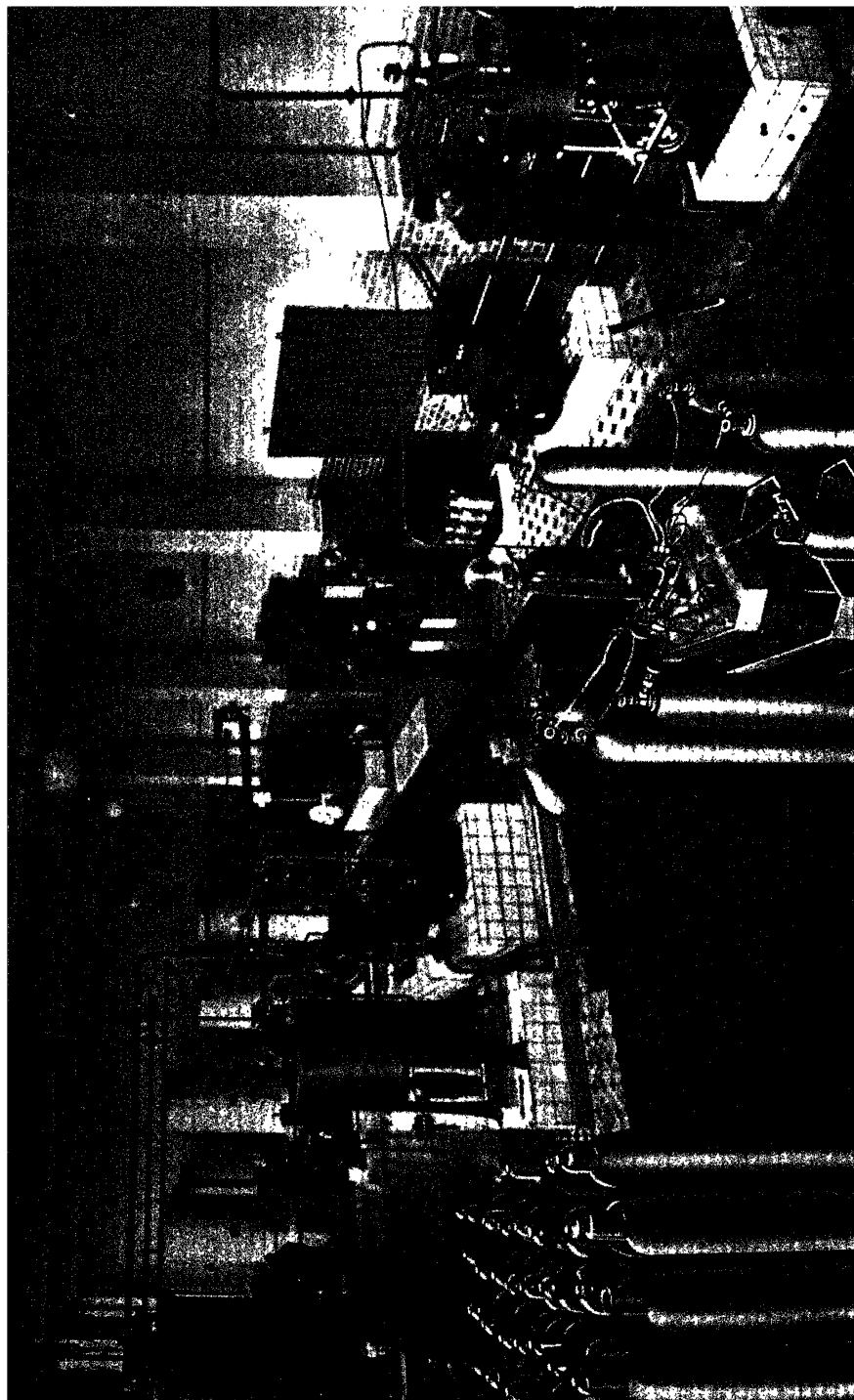


FIG. 142.—Oxycon works in Berlin. Linde system.

simple manœuvre, with this object in view, all the liquid air and all the cold is passed from the frozen column to the other, and the latter is placed in its turn in working order after a comparatively short stoppage.

At the commencement of manufacture, the apparatus is filled with liquid air produced by expanding the air from ~~200~~ atmospheres. With the oxygen *régime*, it is possible to lower the pressure to 50 atmospheres in a plant of 50 cubic metres per hour.

Still more recently Professor Linde has given preference to another method of desiccating the air—the treatment of drying by cold, for which he uses the cold-producing auxiliary machine, of which we have spoken at length, and which obtains in this new connection its complete justification. It is, therefore, in the exchangers themselves fitted for the purpose that the rime is condensed, and when one of the systems of exchangers is blocked, which takes place about every twenty-four hours, a very simple manœuvre substitutes therefor the exchanger in working condition, so that by means of these substitutions the working of the apparatus can be prolonged for twelve days and over.

Fig. 143 represents an installation on the Linde system actually working for M. Bardot in Paris producing 20 cubic metres per hour. Another installation has just been started by M. Bardot at Aubervilliers, near Paris, and this installation, which at present represents the most advanced *oxygen* plant on the Linde system, produces 50 cubic metres per hour.

The most usual apparatus on Claude's system are sizes from 5 to 20 cubic metres, which at present are at work in some forty installations.

Numerous pure nitrogen Linde apparatus working on the principles set forth on p. 395 are furthermore in

affiliated to the *Italian Company for Nitrogen Products*, and in France, notably at Notre-Dame de Briançon (Haute Savoie).

The most powerful apparatus on the Linde system is actually that in use at the Cyanamide Works at Odda in Norway, belonging to Nitrogen Fertilisers, Ltd., turning out pure nitrogen, and capable of an output of ~~375~~ cubic metres of this gas per hour.

**Installations of the Liquid Air Company.**—In the installations fitted up by the *Liquid Air Company* down to the present time, the desiccation of the air is assured by its passage through soda towers, or, following the practice of the *British Oxygen Company*, through baffle boxes filled with hydrated lime, the desiccation, moreover, being further assured by the passing of air under pressure, through recipients filled with chloride of lime. Still more recently Claude has succeeded in utilising the great efficiency of expansion with exterior work to obtain without any other source of cold a desiccation entirely based upon cold. Similar to the Linde system described above, the special exchangers which he has devised for this object, which are otherwise extremely simple, have to be replaced every twenty-four hours, and under these conditions the working of an apparatus is enabled to be worked without interruption during twelve to fifteen days.

The present installations of the *Liquid Air Company* of Paris are based upon the backward return and double rectification, and are working according to what we have termed above, the *single cycle* principle.

The Claude apparatus quite recently attained this last stage. That gives absolute satisfaction from the point of view of results obtained and simplicity of working, after having conquered a difficulty which does not exist when expansion alone without external work is used. It should be clearly understood, moreover, the expansion compen-



sating the loss of cold is carried out in the Claude system with external work. But the air, after expansion, must be liquefied in the bundle of tubes F, F', in Fig. 145, and it is really not the case of heating it up, by first passing it through a liquefier and to bring about liquefaction under pressure, the urgent necessity for which we have demonstrated. We seem, therefore, to be condemned not to use this process of the single cycle, save under conditions where the yield from expansion with external work is unavoidably bad, so Claude therefore practically constructed all his first apparatus on the principle of the double cycle.

Claude was able to overcome this initial defect, and through the single cycle to benefit from the decisive advantages of liquefaction under pressure by means of the following device: The exhaust air is passed immediately on issuing from the machine into the double bundle of pipes F, F', and, instead of confiding the task of provoking liquefaction under pressure thereto, *the very cold nitrogen is entrusted with this function* when just evaporating and issuing through r. Instead, therefore, of sending this nitrogen directly to the exchanger for which it is destined, we make it first traverse the liquefier of the apparatus, whose bundle of pipes is supplied with compressed air at the initial pressure. The liquid air produced is sent with the exhaust air into the collector of the rich liquid.\*

The cooling and filling up of the apparatus are then effected by leaving completely open the valves for the upward delivery of the liquids R, R', so as to do away with all counter-pressure in the machine and take advantage of the total expansion. The temperature of the whole is progressively lowered, and at a given moment liquid air commences to form in the liquefier. The liquid already

\* We can, if we wish, use in a similar way for liquefaction under pressure the cold from the oxygen before sending this into the exchanger.

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formed carried over with the exhaust air is delivered onto the trays of the rectification column and progressively fills the apparatus.

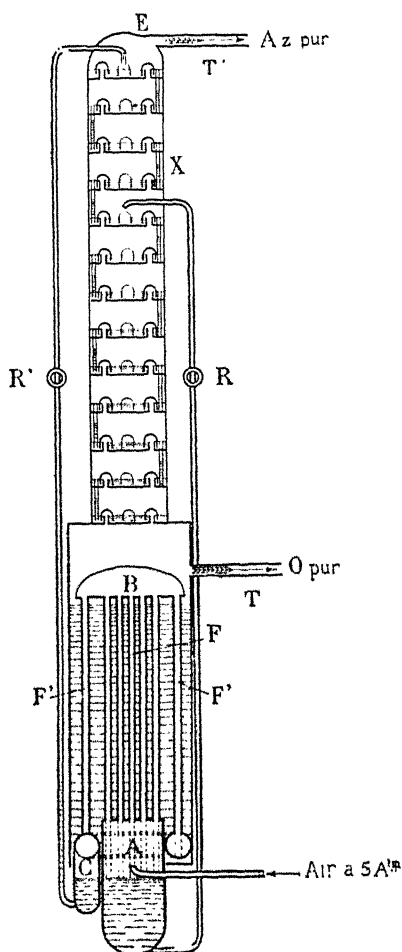


FIG. 145.—Adaptation of the Claude apparatus to working in single cycle.

When the filling up is completed it is sufficient to close the valves for the upward delivery; the exhaust air no longer being able to escape, the pressure rises in the tubular system, and liquefaction is produced; the valve for the upward delivery of the liquid are then adjusted by

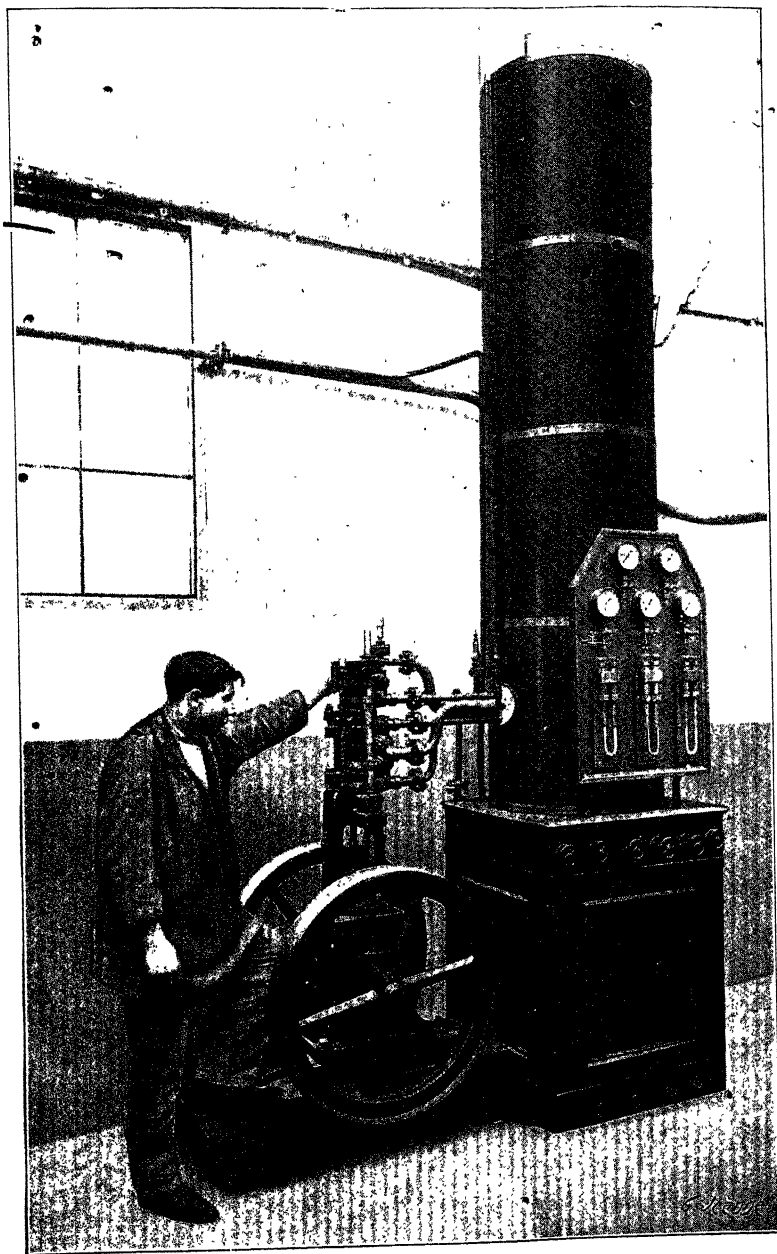


FIG. 146.—Twenty cubic metres per hour unit on the Claude system with single cycle and compound liquefaction constructed for the Bilbao works.

means of the liquid gauges of which we have spoken (p. 319), so as to only deliver the liquid upward as it is formed. The proportion of oxygen thereupon progressively increases; this is controlled by analysis or by a clever automatic apparatus invented by Linde. When the proportion reaches the desired value, say, 96 per cent., the delivery valve is progressively opened to the extent required to maintain the proportion of oxygen, and so that that of the nitrogen on its side remains a minimum. The respective deliveries of compressed air of the two exchangers are at the same time adjusted, according to the readings of the thermometers fixed at the issue of the separated gases. The duration of this starting up is usually from six to seven hours. When manufacturing liquid air, work is carried on naturally with the highest pressure of which the installation is capable—that is, with 35 to 40 atmospheres generally—so as to hasten the filling up. In manufacturing oxygen this pressure is generally higher than is necessary in spite of the counter-pressure, to bring about the addition of the cold and ensure the constant quantity of liquid air in use. The pressure is therefore diminished up to the point where there is no gain in liquid.

In an apparatus for 50 cubic metres of oxygen per hour, the pressure may in this way be lowered down to *twenty-four* atmospheres; it does not exceed *eighteen* atmospheres in a 100 cubic metre apparatus.

It follows from this circumstance that the conditions of expansion are essentially different during the filling up stage and that of normal working. When working with liquid air the ratio of expansion, including the contraction due to expansion, is at least 20 to 1. In working with oxygen it is reduced both by the fact of the lowering of the initial pressure and by that of the increase of the counter-pressure in the vaporiser, which, as we know, is always at least equal to four atmospheres absolute. The ratio of

expansion, in other words, can therefore change from twenty in the first case to four in the second. Now, we have

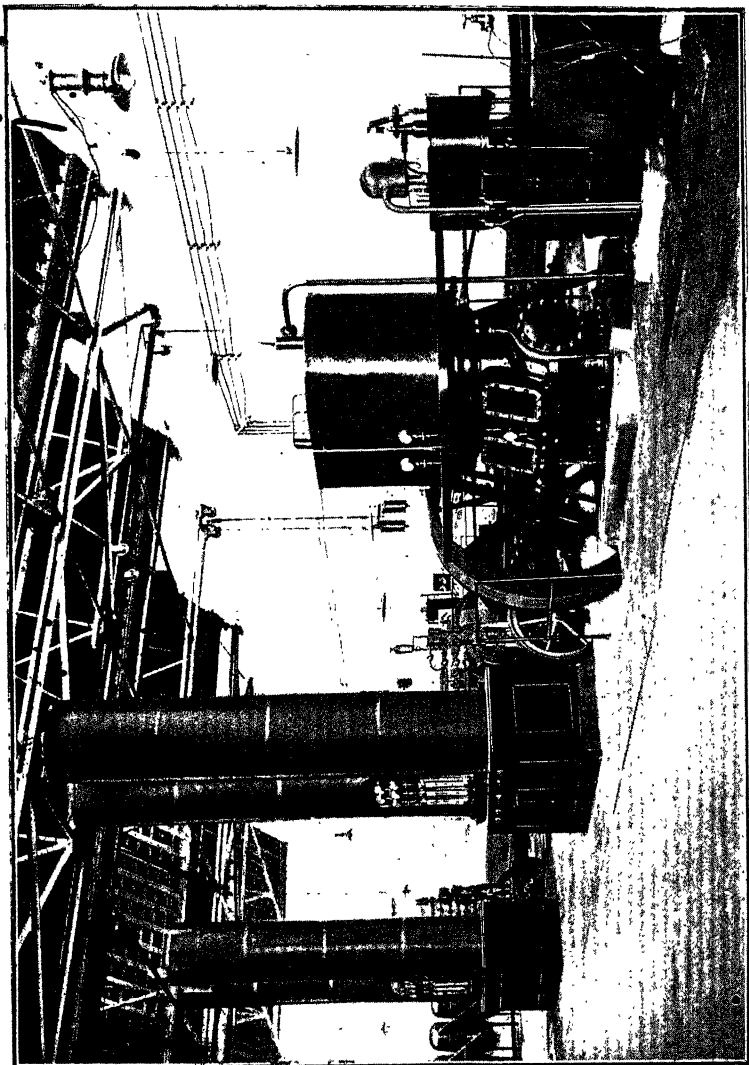


FIG. 147.—Oxygen works near Liège (Belgian Liquid Air Co.)

insisted upon the defects of single expansion with a ratio as high as twenty, so that in working with liquid air it would be very advantageous to work with compound

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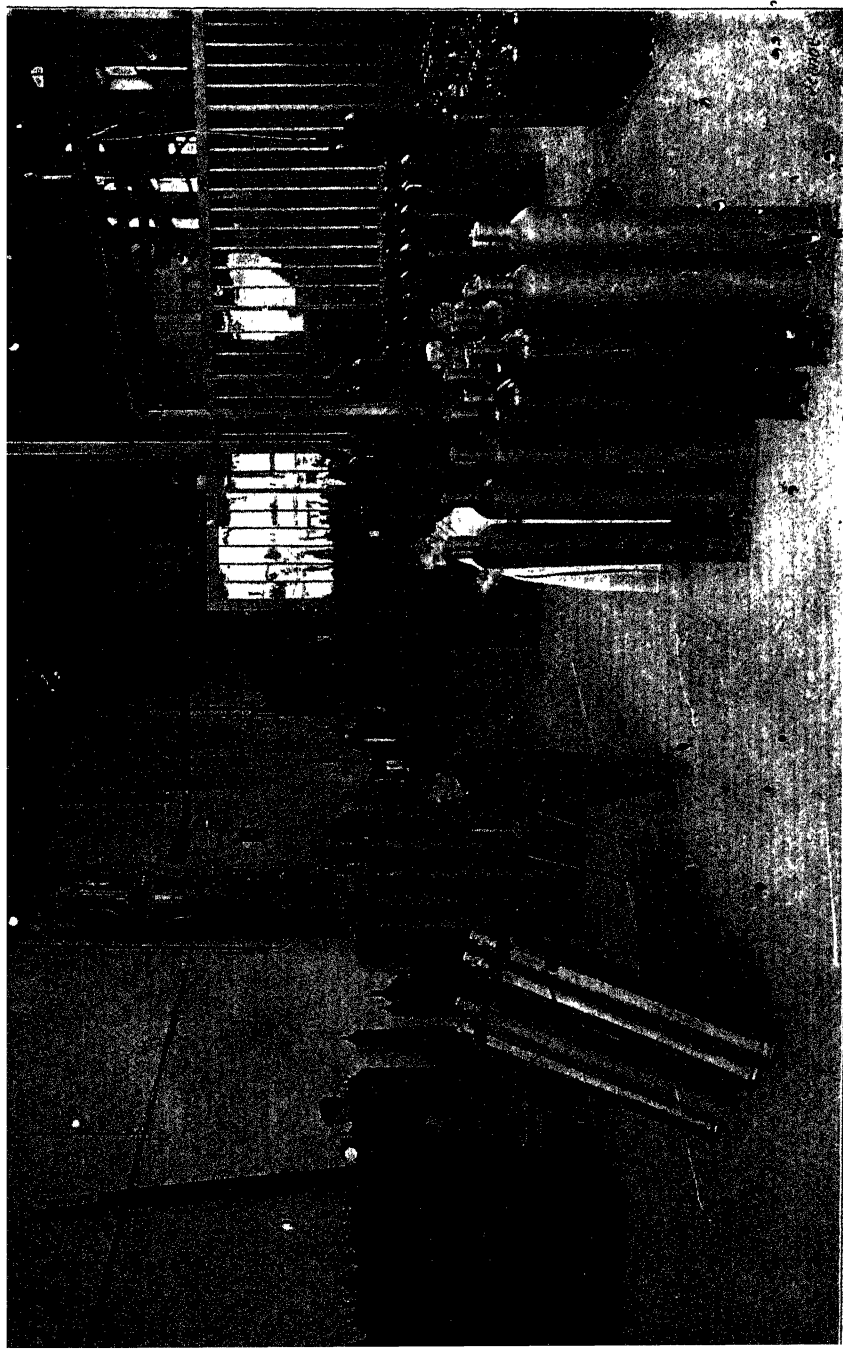


FIG. 148.—Handling flagons of compressed oxygen in the works of the Compressed Gas Co. at Boulogne-sur-Seine.

expansion, while this would be impossible in working with oxygen. Here is the way in which Claude has been able to reconcile the two principles.

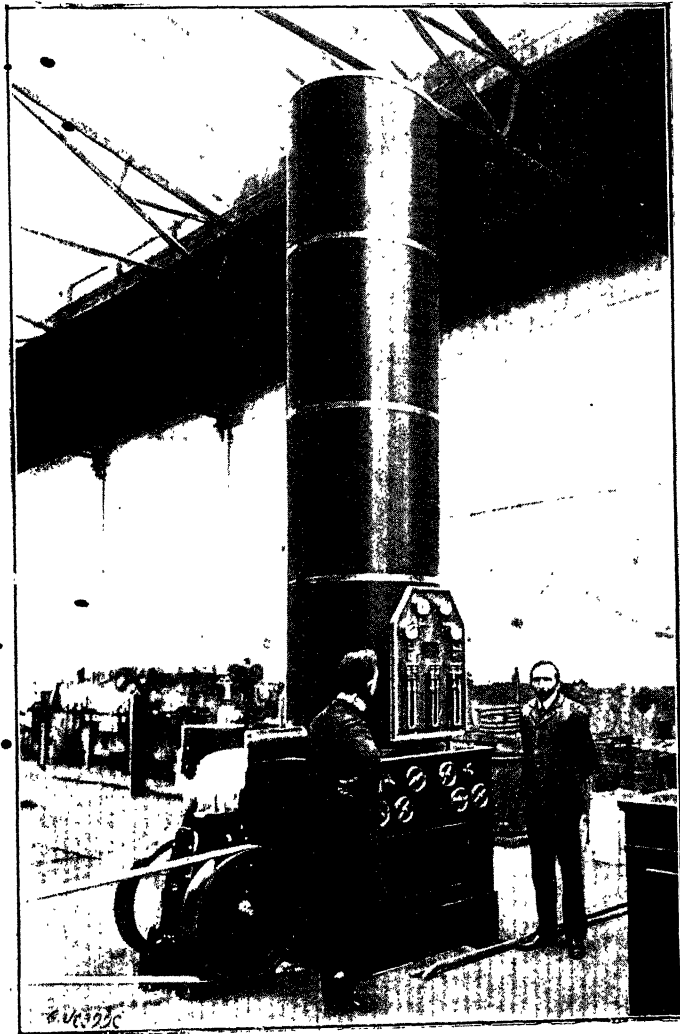


FIG. 149.—Fifty cubic metres per hour unit; present model of the Liquid Air Company.

When the plants are designed to work for long periods the duration of the starting-up with a two hours' margin

matters little. The simplicity of a non-compound machine is to be preferred to the saving of time; if the stoppages, on the contrary, are to be short and frequent the starting-up time becomes very important. We then use a compound machine, which a very simple device permits of decomposing so soon as it is used for the manufacture of oxygen. This device is the one attached to the unit in Fig. 146, capable of an output of twenty cubic metres per hour, and constructed for the oxygen works of Bilbao.

• Fig. 55, p. 183, is a view of a 50 cubic metre apparatus such as the Liquid Air Company at first constructed them. This apparatus comprises externally two columns about 4.50 m. high. The right-hand column contains the exchangers and the liquefier, while the left-hand column contains the apparatus for evaporating and rectification. The works of the *Compressed Gases Company*, at Boulogne-on-Seine, the *Belgian Liquid Air Company's* works at Ougrée, near Liège (Fig. 147), are each furnished with two apparatus of this type.

The Liquid Air Company has recently succeeded in rendering their apparatus more compact without interfering with the ease of erection, and they have combined the whole apparatus in a single column, whose appearance is shown, for a fifty cubic metres per hour plant in Fig. 149. There naturally follows from this arrangement a notable diminution in the penetration of external heat and an appreciable lowering of pressure in working, the reduction of this pressure to the extreme limit constituting, be it understood, a sure criterion of the value of the apparatus from the economic point of view.

It is interesting in this connection to note the lowering of pressure in the following apparatus:

10 cubic metres per hour, the working pressure is 50 atmosphere.					
20	"	"	"	35	"
50	"	"	"	24	"
100	"	"	"	18	"